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HEAT STERILIZABLE,  
IMPACT RESISTANT CELL  
DEVELOPMENT

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CONTRACT NO. 951296

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Edited by GWB  
G. W. BODAMER  
Program Director

Approved by RA Schaefer / GWB  
R. A. SCHAEFER  
Director of Research

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## ABSTRACT

The requirements of this contract were detailed in the Interim Summary Report which reviewed all the work from September 24, 1965 to September 30, 1967. The present report covers work during the period October through December 1967.

Impact specifications have been changed to require survival of shock at  $2800 \pm 200$  "g" from a velocity of  $115 \pm 3$  ft./sec. In addition, new heat sterilizable battery capabilities have been required and can be summarized as follows.

1. a. 5 AH, 120 WH,  $2800 \pm 200$  "g" from  $115 \pm 2$  ft./sec.,  
4 cycles thereafter.  
b. 25 AH, 600 WH,  $2800 \pm 200$  "g" from  $115 \pm 2$  ft./sec.,  
4 cycles thereafter.
2. 1200 WH, non-impact, 400 cycles of 50% depth.
3. 2000 WH, 200 "g" impact, 4 cycles thereafter.

Studies during the last quarter of 1967 have revealed the following facts. A prolonged low current pre-formation charge virtually eliminates the pressure build-up previously encountered during formation. A partial discharge followed by recharge at the end of normal charge increases capacity 15%. This technique, however, is not sufficient to overcome capacity losses which follow sterilization of sealed cells and which run between 20 and 60%. Five amp-hr sealed cells with silver sheet electrode reinforcement have survived 2000 to 2400 "g" shocks but show a 30% loss in capacity thereafter; however, the loss is recovered upon recharging.

Future work will be concentrated on determining the cause of capacity loss following heat sterilization and on making more strongly reinforced plates.

## TABLE OF CONTENTS

Abstract . . . . .	i
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### ELECTROCHEMISTRY

I.	Introduction . . . . .	1
II.	Optimization Studies . . . . .	1
III.	Effects of Organic Constituents on Silver-Zinc Cells . . .	20
IV.	Grid Supports . . . . .	20
V.	Absorber Studies . . . . .	26
VI.	Mixing of Active Materials . . . . .	28

### FABRICATION AND TESTING OF CELLS

I.	Fabrication and Testing of 25 AH Cells . . . . .	31
II.	Heat Sterilizable-High Impact 5.0 AH Cells . . . . .	34
III.	Development of Heat Sterilizable High Impact 5 and 25 AH Batteries. . . . .	46
IV.	Development of Heat Sterilizable Non Impact High Cycle Life 1200 WH Battery . . . . .	48
V.	Development of Heat Sterilizable 200 "G" Impact 2000 WH Battery. . . . .	50
	Appendix . . . . .	57
	Conclusions . . . . .	59
	Future Work . . . . .	59

# LIST OF TABLES

Table I	Summary of Pressure Data on Sterilized Then Sealed Ag-Zn Cells . . . . .	2
Table II	Summary of Cell Capacities for Sterilized Then Sealed Ag-Zn Cells . . . . .	3
Table III	Performance-Pressure Data on Sterilized Then Sealed Ag-Zn Cells . . . . .	4
Table IVA	Performance of Sealed Then Sterilized Ag-Zn Cells at 300 ma/sq. in. . . . .	6
Table IVB	Performance of Sealed Then Sterilized Ag-Zn Cells at 300 ma/sq. in. . . . .	7
Table V	Additional Cycles on Cells Having Differing Electrolyte Concentrations . . . . .	9
Table VI	Performance of Cells Having 3% Compound 323-43 in Negatives and 35% KOH Electrolyte . . . . .	10
Table VII	Effect of Amount of 323 in Negative Electrodes on Cell Capacity. . . . .	12
Table VIII	Increase in Capacity by Partial Discharge During Charge on Cells Which Have Been on Float and on Stand . . . . .	14
Table IXA	Effect of Pre-formation Mode on Cell Pressures in Ag-Zn Cells Containing Compound 323-43 . . . . .	16
Table IXB	Effect of Pre-formation Mode on Cell Pressures in Ag-Zn Cells Containing Compound 323-43 . . . . .	17
Table X	Capacities of High Performance Cells . . . . .	19
Table XI	Capacity of Various Series of Sealed Ag-Zn Cells in the Presence of Organics . . .	21
Table XII	Overpotentials of Negative Grid Supports. . . . .	24

## LIST OF TABLES (continued)

Table XIII	Overpotentials of Positive Grid Supports . . . . .	.25
Table XIV	Capacity (AH) of Sealed Cells with Zr Supports in Both Plates . . . . .	.27
Table XV	Overvoltage Data on the Mixing Time of Negative Materials . . . . .	.30
Table XVI	Properties of Plate Reinforcing Materials . . . . .	.32
Table XVII	Shock Data for Model 344 Test Cells. . . . .	.35
Table XVIII	Effect of 2800 "G" Impact on Capacity in 5 AH Sealed Non Sterile Cells . . . . .	.36
Table XIX	Effect of Heat Sterilization and Cycling on A. C. Impedance of 5.0 AH Sealed Cells . . . .	.39
Table XX	Operating Capacities and Voltages After Heat Sterilization 120 Hours at 125°C Model 344 5.0 AH Cells . . . . .	.40
Table XXI	Effect of High Impact on Model 344 5 AH Cells . . . .	.43
Table XXII	Electrolyte Absorption of Sterile and Non Sterile Separator Lots (RAI-116 and SWRI-GX) . . . . .	.45
Table XXIII	Water Loss from Model 344 Cells During Heat Sterilization . . . . .	.47
Table XXIV	Experimental HSS48 Cell Test Variabels. . . . .	.53
Table XXV	Weight Analysis and Estimated Output 80 AH Heat Sterilizable 200 "G" Impact Cell ESB Model 364 . . . . .	.55
Table XXVI	Physical Characteristics Heat Sterilizable Membranes . . . . .	.58

## LIST OF FIGURES

### ELECTROCHEMISTRY

Figure 1	Teflon Case in Nickel Bomb . . . . .	22
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### FABRICATION AND TESTING OF CELLS

Figure 1	Decrease in Load Voltage from 2870 "G" Shock on 5 AH Cells . . . . .	37
Figure 2	Capacity Loss from Wet Heat Sterilization and High Impact in 5 AH Cells . . . . .	42
Figure 3	Typical Design of High Impact 5 AH and 25 AH Batteries Nine-Cell Unit 2500 "G" Shock . . . . .	49
Figure 4	Performance of 25 AH Heat Sterilizable Non-Impact Cells . . . . .	51
Figure 5	Effect of Discharge Rate on Performance of 25 AH Sterile Sealed Cell (Heat Sterilized 120 Hours at 125°C) . . . . .	52
Figure 6	Development Model 364 Heat-Sterilizable HSS80 Ag-ZnO Cell . . . . .	54

## ELECTROCHEMISTRY

### I. INTRODUCTION

The requirements for a high energy density cell - either silver-zinc or silver-cadmium - which could be heat sterilized in the sealed but unformed condition, formed, impacted as in a hard planetary landing, and function thereafter through four discharge-charge cycles have been discussed in previous reports on Contract 951296. The present report, for the Fourth Quarter of 1967, deals mainly with total cell performance and with the problem of grid reinforcement.

### II. OPTIMIZATION STUDIES

Since the last report several cell parameters have been under consideration. Among the more significant ones were electrolyte concentration, pack tightness, percent of Compound 323-43 in the zinc electrode, and charging regimes. Details of individual variables as well as combinations of variables in the form of complete cells and batteries are reported in this section.

#### A. Effect of Electrolyte, Compound 323-43, and Pack Tightness on Cell Performance

Cumulative capacity and pressure data are shown in Tables I, II, and III for cells sterilized and then sealed. Variables studied included effects of electrolyte concentration, pack tightness, and per cent of Compound 323-43 in the zinc electrode. Most of the cells in the study had electrolyte concentrations of either 35% KOH or 41% KOH, both determined before saturation with ZnO. The ZnO concentrations were seventy-five gms per liter for 35% and 110 gms/per liter for 41%. Pack tightness varied from  $2.1 \times 10^{-3}$  to  $2.6 \times 10^{-3}$  inches per layer of expanded thickness of the separator. Three cells from each group of cells of similar construction were made into batteries after several cycles and cycled as batteries. Pressures and capacities for the early cycles were averages. These averages are included in Table III.

The important conclusions are presented below. For 35% KOH electrolyte: (1) cell capacities tend to increase during several cycles before reaching their maximum, generally at the 3rd or 4th cycle; (2) cell pressures tend to increase during several cycles before leveling off at a value where they tend to remain or decrease slightly; (3) higher capacities result in cells having the smaller per cent of Compound 323-43. For 41% KOH electrolyte: (1) in the more loosely packed cells, a decrease in capacity results between the first and second cycle, then tends to increase during the third or fourth cycle, and continues to increase slowly for several cycles before approach-



TABLE I  
Summary of Pressure Data on Sterilized Then Sealed Ag-Zn Cells

Cell No.	A	B	C	D	Formation	2nd	3rd	Pressure in psig at end of charge:					9th
								4th	5th	6th	7th	8th	
191	40	2.5	3	0	2.5	10.7	15.7	18.0	-	5.7	5.5		
192	35	2.5	3	0	7.0	12.5	17.9	18.2	-	8.7	7.5		
193	35	2.5	3	3	5.9	6.2	9.0	10.4	12.0	14.1	13.6	12.5	13.5
194	35	2.5	3	3	6.5	12.8	15.6	15.8	19.5	21.1	23.3	21.3	22.7
195	35	2.5	3	0	7.0	11.5	15.8	18.0	19.6	21.3	19.3	9.9	10.7
197	35	2.5	3	0	8.0	18.2	10.0	21.0	22.0	23.8	22.8	15.1	16.0
196	40	2.5	3	0	3.0	3.0	4.1	3.8					
199	35	2.6	7	2	8.0	8.0	9.0	9.5	11.1	13.0			
200	35	2.6	7	2	3.1	5.9	7.0	8.0	8.0	10.0	11.8		
201	35	2.6	7	2	0.8	2.1	3.2	4.2	5.8	5.9	7.1	8.0	
202	35	2.6	7	2	6.5	7.5	7.1	7.5	9.8	9.6	10.4	10.8	
204	35	2.6	7	2	4.1	5.2	6.1	5.0	7.5	7.0	8.4	9.1	
205	41	2.6	7	2	18.9	-	15.0	-	12.6	7.3	7.9		
206	41	2.6	7	2	1.9	-	2.2	-	2.2	2.8	3.4		
208	41	2.6	7	2	-0.3	2.3	2.5	2.9	2.9	2.7	3.0	2.5	
209	41	2.6	7	2	1.0	2.3	1.2	4.0	1.8	-	2.1	1.9	
210	41	2.6	7	2	6.9	5.8	6.1	5.0	5.0	4.5	4.7	4.1	
211	35	2.6	7	2	2.9	4.6	6.0	5.5					
212	35	2.6	7	2	-0.7	0	-0.5	-0.3					
213	41	2.1	7	2	1.0	1.5	1.5	2.0	2.5				
214	41	2.1	7	2	3.6	4.8	4.5	3.9	4.3				
215	41	2.1	7	2	0.5	0.5	1.2	1.5	2.2				
216	41	2.1	7	2	1.5	2.0	2.3	3.0	4.0				
217	35	2.1	7	2	1.0	4.0	4.5	5.3	6.0				
218	35	2.1	7	2	7.0	10.8	10.8	10.9	11.1				
219	35	2.1	7	2	1.0	2.3	1.8	2.6	2.9				
220	35	2.1	7	2	2.1	3.2	3.8	4.5	5.1				

A - Electrolyte concentration before saturation with ZnO (%).  
 B - Pack tightness (in. per layer of separator x 10<sup>-3</sup>).  
 C - Percent Compound 323-43 in negative electrode.  
 D - Percent Teflon in Negative electrode.

TABLE II  
Summary of Cell Capacities for Sterilized Then Sealed Ag-Zn Cells  
Amp-hr for Discharge No.

Cell No.	A	B	C	D	1	2	3	4	5	6	7	8	9
191	40	2.5	3	0	5.68	5.94	5.85	5.73	6.44	6.73	7.11	7.20	7.11
192	35	2.5	3	0	5.60	5.54	5.52	5.59	6.37	7.15	7.45	7.32	7.18
193	35	2.5	3	3	4.93	5.53	6.45	6.71	6.22	6.65	7.23	6.71	6.75
194	35	2.5	3	3	5.47	6.66	6.96	6.95	6.68	6.79	6.95	6.39	6.84
195	35	2.5	3	0	7.02	6.48	7.07	6.84	6.12	6.40	7.05	6.96	7.08
197	35	2.5	3	0	5.63	6.53	6.76	7.18	5.97	6.51	7.29	7.27	7.42
196	40	2.5	3	0	6.84	6.96	6.86	6.94					
199	35	2.6	7	2	5.92	6.19	6.00	5.97	6.08	6.24			
200	35	2.6	7	2	5.76	6.35	6.51	6.51	6.35	6.24			
201	35	2.6	7	2	5.90	5.66	6.06	6.13	6.24	6.01	6.36	6.24	
202	35	2.6	7	2	5.14	5.76	6.21	6.39	6.24	6.01	6.37	6.24	
204	35	2.6	7	2	6.25	5.86	6.15	6.31	6.24	6.01	6.15	6.24	
205	41	2.6	7	2	5.60	4.93	5.32	5.43	5.69	5.76			
206	41	2.6	7	2	6.19	5.32	5.35	5.47	5.60	5.90			
208	41	2.6	7	2	6.12	5.47	5.61	5.97	5.68	5.70	5.90	5.79	
209	41	2.6	7	2	5.75	5.74	5.74	6.22	5.68	5.70	6.00	5.79	
210	41	2.6	7	2	6.00	5.55	5.40	5.76	5.68	5.70	5.76	5.79	
211	35	2.6	7	2	5.31	5.87	6.15						
212	35	2.6	7	2	5.90	6.12	6.21						
213	41	2.1	7	2	5.70	5.91	5.83	5.83	6.00				
214	41	2.1	7	2	5.88	6.05	5.60	5.97	5.68	5.55			
215	41	2.1	7	2	5.63	5.90	5.60	5.83	5.79	5.55			
216	41	2.1	7	2	5.51	5.79	5.65	5.63	5.67	5.55			
217	35	2.1	7	2	5.36	5.66	5.74	6.00	5.70				
218	35	2.1	7	2	5.35	5.43	5.68	5.95	5.90	5.71			
219	35	2.1	7	2	5.77	6.06	5.95	6.09	6.17	5.71			
220	35	2.1	7	2	5.90	5.89	6.03	5.85	6.07	5.71			

A - Electrolyte conc (% KOH) before saturation with ZnO.

B - Pack tightness (in. per layer of separator x 10<sup>-3</sup>).

C - % Compound 323-43 in negative electrode.

D - % Teflon in negative electrode.

TABLE III

Performance-Pressure Data on Sterilized Then Sealed Ag-Zn Cells

Battery of Cells Numbered:	201-202-204	218-219-220	208-209-210	214-215
Electrolyte concentration (before ZnO addition)	35	35	41	41
Pack tightness (in/layer sep)	0.0026	0.0021	0.0026	0.0021
Performance, amp-hr				
Formation charge	7.15	6.79	6.55	6.28
First discharge (100 ma/sq. in.)	5.19	4.86	4.68	4.59
Total	5.76	5.67	5.96	5.67
Second discharge (100 ma/sq. in.)	5.27	5.23	4.94	4.92
Total	5.76	5.79	5.58	5.91
Third discharge (100 ma/sq. in.)	5.49	5.35	4.98	4.95
Total	6.14	5.88	5.58	5.62
Fourth discharge (100 ma/sq. in.)	5.79	5.37	5.31	4.97
Total	6.27	5.96	5.95	5.81
Fifth discharge (100 ma/sq. in.)	(1) 5.76	5.45	(1) 5.40	5.04
Total	(1) 6.24	6.05	(1) 5.68	5.71
Sixth discharge (100 ma/sq. in.)	(1) 5.58	(1) 5.31	(1) 5.20	(1) 4.80
Total	(1) 6.01	(1) 5.71	(1) 5.70	(1) 5.55
Seventh discharge (100 ma/sq. in.)	5.36		5.18	
Total	6.29		5.88	
Eighth discharge (100 ma/sq. in.)	(1) 5.76		(1) 5.31	
Total	(1) 6.24		(1) 5.79	
Pressure, psig, average				
End of formation	3.8	3.8	2.6	1.8
End of first recharge	4.9	4.7	3.9	2.5
End of second recharge	5.4	5.4	3.3	2.6
End of third recharge	5.5	6.0	3.9	2.8
End of fourth recharge	7.5	6.3	3.2	3.5
End of fifth recharge	7.5	6.3	-	3.0
End of sixth recharge	8.6		3.3	
End of seventh recharge	9.3		2.8	

(1) Capacities represent battery performances; all others represent average of single cell capacities.

ing the capacities obtained during the first cycle; (2) in the tightly packed cells, capacities during the second cycle tend to be slightly higher than the first, and tend to remain at approximately this value for the next several cycles; (3) pressure increases during cycling tend to remain near the value reached at the end of formation. Comparing 35% KOH and 41% KOH electrolytes: (1) for similar pack tightness, cells having 35% KOH tend to yield higher capacities and have higher load voltages than those having 41% KOH; (2) maximum pressures tend to be higher in cells having 35% KOH than in those having 41% KOH; (3) for the two-step discharge, at rates of 100 ma per sq. in. and 20 ma per sq. in., higher percentages of total capacities are obtained at the higher discharge rate in cells having 35% KOH than in those having 41% KOH.

Other observations: (1) higher percentages of the recharge capacity before the partial cycle occurs in cells having 35% KOH than in those having 41% KOH electrolytes; (2) silver oxide penetration through the separator tends to be more rapid in 35% KOH cells than in 41% KOH cells. The latter would be expected, based on diffusion rates and was verified when two cells, 203 and 207 were dissected after four cycles. In cell 203, having 35% KOH, silver oxide had penetrated to the third layer of separator removed from the silver electrode, but in cell 207 having 41% KOH, penetration had been confined to the first layer of separator.

To study further the effect of some of the above variables on rate capabilities of cells, several cells were discharged at 300 ma per sq. in. as presented in Tables IV A and B. This discharge rate was actually about three times as great as the usual rate. Discharges were continued to end-of-load voltages of 1.20. The conclusions follow: (1) no significant capacity effect of electrolyte concentration in the range studied was noted; (2) no significant effect of percentage of Compound 323-43 resulted; (3) best overall performance was obtained from cell 229 which contained no polypropylene absorber or retainer.

Not adequately explained at present is the reason for the apparent rise in electrolyte level during formation. In silver-zinc cells having wrapped positive electrodes an electrolyte level rise is expected, and adequate explanations have been advanced. In these cells having wrapped zinc electrodes it would not be expected, based on the explanation for its rise in positive-wrapped cells. The rise begins after the cell reaches 1.40 volts during formation at the same time as the pressure increase commences. Probably, the electrolyte is forced out of the negative electrode by the gas generated there. Why it remains at the high level during subsequent cycles is not known.

#### B. Effect of Charging Regime on Cell Capacity

It has been observed that if, after recharging a cell, a partial discharge was run (generally, 0.9 amp hr.) was removed at 1.8 amp and this was followed by a recharge at the formation rate, an increase in capacity occurred during the subsequent discharge, and capacity variation among

TABLE IV A

Performance of Sealed Then Sterilized Ag-Zn Cells at 300 ma/sq. in.

Cell Number	93	94	95	97	96
Dischg. at 5.4 amp.					
Voltage after ____ min.					
1 min.	1.415	1.428	1.403	1.465	1.369
2 "	1.395	1.411	1.384	1.455	1.344
4 "	1.370	1.388	1.358	1.424	1.306
8 "	1.327	1.349	1.311	1.380	1.250
12 "	1.288	1.313	1.277	1.359	1.214
16 "	1.265	1.293	1.254	1.315	1.209
20 "	1.257	1.285	1.250	1.298	1.210
24 "	1.256	1.284	1.250	1.292	1.197
28 "	1.258	1.286	1.254	1.293	
32 "	1.259	1.288	1.254	1.310	
36 "	1.259	1.290	1.253	1.297	
40 "	1.258	1.289	1.247	1.296	
44 "	1.260	1.286	1.239	1.308	
48 "	1.250	1.280	1.225	1.302	
52 "	1.230	1.271	1.204	1.310	
56 "	1.219	1.256		1.272	
60 "		1.232		1.256	
64 "				1.229	
Cycle Number	10	10	10	10	5
Amp-hr to 1.30 volts	0.90	1.26	0.90	1.62	0.36
Amp-hrs to 1.20 volts	5.22	5.67	4.86	5.94	1.98
Electrolyte concentration					
before ZnO saturation	35	35	35	35	40
Per cent Compound 323-43	3	3	3	3	3

TABLE IV B  
Performance of Sealed Then Sterilized Ag-Zn Cells at 300 ma/sq. in.

Cell Number	199	200	205	206	213	217	229
Electrolyte concentration, % KOH	35	35	41	41	41	35	41
Pack tightness (in./layer sep. $\times 10^{-3}$ )	2.6	2.6	2.6	2.6	2.1	2.1	2.5
Voltage after _____ minutes at 5.4 amps							
1 min.	1.397	1.445	1.460	1.506	1.570	1.415	1.509
2 "	1.377	1.422	1.422	1.488	1.540	1.394	1.492
4 "	1.354	1.392	1.416	1.451	1.513	1.360	1.461
8 "	1.320	1.347	1.374	1.403	1.458	1.313	1.403
12 "	1.310	1.329	1.352	1.380	1.402	1.290	1.374
16 "	1.300	1.317	1.320	1.347	1.350	1.284	1.370
20 "	1.295	1.311	1.282	1.301	1.271	1.272	1.366
24 "	1.285	1.308	1.296	1.290	1.266	1.260	1.362
28 "	1.278	1.305	1.267	1.276	1.260	1.251	1.357
32 "	1.271	1.303	1.273	1.272	1.254	1.240	1.353
36 "	1.264	1.300	1.270	1.265	1.246	1.229	1.348
40 "	1.252	1.297	1.265	1.259	1.235	1.217	1.343
44 "	1.235	1.290	1.259	1.248	1.219	1.201	1.338
48 "	1.250	1.281	1.247	1.228	1.199		1.330
52 "		1.267	1.225				1.321
56 "		1.235					1.307
60 "		1.200					1.287
							1.261
							1.214
Cycle number	7	7	7	7	6	6	3
Amp-hrs to 1.30 volts	1.62	3.24	1.62	1.80	1.44	0.90	5.22
Amp-hrs to 1.20 volts	4.32	5.40	4.86	4.77	4.32	4.05	6.12

(1) All cells contained 6 layers of SWRI-GX separation.

(2) All cells except 229 had EM476 retainers around negative electrode and w-fold around positive electrode.

No. 229 had no EM476 but had a GX separator retainer.

cells diminished. This effect is noticeable for cells 187-188-189-190 during the fifth discharge, and for all cells during the seventh as shown in Table V. Comparing those two discharges with the sixth and eighth, the effect is obvious. Additional data on this phenomenon are included on Table VI for cells 191-197 during the third, fourth, and sixth discharge and the capacity increase during the sixth discharge for cells 191 and 192. In Table VII, the effect was observed during the fifth discharge of cells 185 and 186. Also in Table VIII supporting data is provided during the most recent discharge of cells 103, 104, 112, and 113. For cells 199-210 (Tables IX A and B) the partial cycle was run at the end of formation and the results were consistent with that reported above. This partial cycle is being included in the cycling regime for all cells henceforth.

An unusual phenomenon was observed during the recharge portion of the partial cycle. If a normal silver-zinc cell (not containing Compound 323-43) is similarly discharged so that the cell potential does not decay to the argentous oxide-zinc level, and then recharge is started, the cell potential almost immediately rises to a value of 1.90 volts or higher. When cells containing Compound 323-43 are similarly treated, the charge voltage remains between the values of 1.83 and 1.89 volts for several hours and for these cells more capacity is returned than had been removed thus accounting for the capacity increase. Apparently, some detrimental effect caused by Compound 323-43 is overcome by this technique. This partial cycle is being included in the cycling regime of cells for which optimum capacity is desired.

#### C. The Effect of Charging Regime on Cell Pressure

To minimize the amount of gas generated during formation, various charging techniques were used. All of them were based on a slow initial charge. First a constant potential float charge was used. It was determined that 1.40 volts was about the highest float voltage that could be used without generating gas. Cells 199 through 205, listed in Tables IX A and IX B, were preformed at different voltages and current limits to establish this. Varying pressures resulted with one being as high as 37.8 in. Hg. Even though the charge current decayed to a fraction of a milliamper, much gas was evolved if the normal formation charge was started before a considerable number of hours on float had elapsed. Also the problems associated with floating a battery of cells at 1.40 volts per cell made this technique undesirable. Consequently, the change to constant current was made.

It was empirically determined that a preformation charge rate of 0.55 ma per square inch was required for not less than 24 hours with 28 to 33 hours being preferred. Beginning with cell 206 through cell 210 in the above mentioned tables, a constant current mode of charge was used to establish this. The equipment did not maintain a truly constant current and at times it varied as much as 3 ma from the desired value. However, cells pre-charged at 10 ma ( $0.55 \text{ ma/in.}^2$ ) in excess of 24 hours had the lowest pressures after the regular formation charge.

TABLE V  
Additional Cycles on Cells Having Differing Electrolyte Concentrations

Cell Number	177	178	187	188	189	190	182
Fourth discharge Amp hrs	5.95	6.40	5.54	5.18	5.58	5.50	5.79
Recharge (ma/sq. in) Amp hrs	6.5	6.5	6.5	6.5	6.5	6.5	6.5
Amp hrs after partial cycle	-	-	5.83	5.66	6.41	6.19	-
	-	-	6.63	6.56	7.11	7.09	-
Fifth discharge Amp hrs	5.95	5.94	6.44	6.44	6.70	6.74	7.02
Recharge (ma/sq. in) Amp hrs	CP 1.96	CP 1.96	6.5	6.5	6.5	6.5	CP 1.96
	-	-	6.0	5.66	6.30	6.0	-
Sixth discharge Amp hrs.	5.40	6.51	5.58	5.18	6.22	5.65	6.98
Recharge (ma/sq. in) Amp hrs	6.18	6.01	5.28	4.92	5.56	5.17	6.12
Amp hrs after partial cycle	6.51	6.33	6.00	5.76	6.24	5.78	6.76
Seventh discharge Amp hrs	6.65	6.73	6.31	6.19	6.19	5.87	7.12
Recharge (ma/sq. in) Amp-hrs	6.00	5.88	5.38	5.05	5.64	4.95	6.09
Eighth discharge Amp-hrs	5.26	5.18	5.11	4.89	5.58	4.77	6.53

- (1) Electrolyte: 177-178, 42% KOH with 110 gm ZnO/liter; 187-188, 40% KOH with 105 gm ZnO/liter; 189-190, 35% KOH with 75 gm ZnO/liter.  
 (2) Separation: 6 layers SWRI GX, 0.0036 in/layer in cell design.



TABLE VI  
Performance of Cells Having 3% Compound 323-43 in Negatives and 35% KOH  
Electrolyte

Cell Number	191	192	193	198	195	194	197
Pre-formation mode (CPl. 382 for all cells)							
Current limit	C/1.5	C/1.5	C/1.8	C/1.8	C/3.2	C/1.3	C/1.3
Hours	48	48	48	48	96	48	48
Final current (ma)	0.2	0	0.14	0.14	0.1	0.3	0.2
Final pressure (in.Hg g)	-2.3	-1.0	-2.0	-2.0	0.6	1.0	0
Formation charge (ma per sq. in)							
	5.5	5.5	8.3	8.3	5.6	5.6	5.6
Amp hrs	6.9	6.8	5.9	7.0	7.6	6.5	6.4
Pressure at end (in.Hg g)	5.0	14.0	12.4	16.0	15.2	17.0	12.8
First discharge							
Amp hrs	5.68	5.60	4.93	6.35	7.02	5.47	5.63
Recharge							
Amp hrs	5.70	5.10	5.7	6.4	6.3	6.6	6.2
Pressure at end (in.Hg g)	21.0	25.0	12.4	19.0	23.0	25.6	36.4
Second discharge							
Amp hrs	5.94	5.54	5.53	6.73	6.48	6.86	6.53
Recharge							
Amp hrs	5.86	5.50	5.60	6.38	6.36	6.3	5.95
Amp hrs after partial cycle -	-	-	6.45	7.06	7.21	6.95	6.65
Pressure at end (in.Hg g)	314.	35.8	18.2	24.4	31.8	31.6	40.0
Third discharge							
Amp hrs	5.85	5.52	6.45	7.05	7.07	6.96	6.76

TABLE VI (continued)  
Performance of Cells Having 3% Compound 323-43 in Negatives and 35% KOH Electrolyte

Cell Number	191	192	193	198	195	194	197
Recharge							
Amp hrs	6.0	5.2	6.52	5.98	6.10	6.21	5.77
Amp hrs after partial cycle	-	-	7.27	6.80	6.72	6.70	6.46
Pressure at end (in Hg g)	36.0	36.4	20.8	24.6	36.2	33.6	42.0
Fourth discharge							
Amp hrs	5.73	5.59	6.71	6.87	6.84	6.95	7.18
Recharge							
Amp hrs	6.28	5.55	5.72	5.49	5.71	6.12	5.73
Amp hrs after partial cycle	6.80	6.55	none	none	none	none	none
Pressure	-	-	24.0	25.0	39.2	39.0	44.0
Fifth discharge							
Amp hrs	6.44	6.37	6.22	5.87	6.12	6.68	5.97
Recharge							
Amp hrs	not recorded	not recorded	5.75	5.29	5.61	6.56	5.58
Amp hrs after partial cycle	not recorded	not recorded	6.18	6.23	6.25	7.02	6.39
Pressure at end (in Hg g)	25.0	28.0	28.2	27.6	42.6	42.2	47.6
Sixth discharge							
Amp hrs	6.73	7.15	6.65	(7) 7.18	6.40	6.79	6.51

(1) Between recharge and partial cycle, one month had elapsed.

(2) Electrolyte concentration: 35% KOH containing 75 gm/liter ZnO except No. 191 which had 40% KOH with 105 gm ZnO/liter.

(3) Separator for all cells: 6 layers SWRI-GX.

(4) Pack tightness: 0.0026 in/layer separator.

(5) Cells 191-192 had mercury plated grids in negative electrodes.

(6) All cells contained 3% Compound 323-43 in negative electrodes.

(7) Cell 198 discontinued because it had been overcharged at 1.8 amp for sufficient time to cause leakage.

TABLE VII  
Effect of Amount of 323-43 in Negative Electrodes on  
Cell Capacity

Cell Number	185	186
Pre-formation mode	CP 1.35	CP 1.35 v
Final current (ma)	0.06	0.06
Final pressure (in Hg g)	1.6	0
Hours	120	120
Formation charge c - 5.5 ma/sq. in		
Amp hrs	7.2	7.0
Pressure (in Hg g)	21.2	4.2
First discharge		
Amp hrs	5.38	5.61
Recharge at 6.5 ma/sq. in	-	-
Pressure (in Hg g)	-	14.4
Second discharge		
Amp hrs	6.35	6.53
Recharge at 6.5 ma/sq. in		
Amp hrs	6.51	6.76
Pressure (in Hg g)	34.0	32.8
Third discharge		
Amp hrs	6.40	6.44
Recharge at 8.3 ma/sq. in to 2.02 v then at 4 ma/sq. in to 2.02 v		
Amp hrs	6.34 + 0.35	6.32 + 0.34
Pressure (in Hg g)	31.8	32.0

TABLE VII (continued)  
Effect of Amount of 323-43 in Negative Electrodes on  
Cell Capacity

Cell Number	185	186
Fourth discharge Amp hrs	6.44	6.44
Recharge at 6.5 ma/sq. in	6.36	6.38
Net gain after partial cycle	0.45	0.45
Total	6.81	6.83
Open circuit one month		
Net gain after partial cycle	0.31	0.85
Total	7.2	7.68
Fifth discharge Amp hrs	7.16	6.80

NOTES: (1) Cells contained 3% Compound 323-43.

(2) Cells contained 40% KOH with 105 gm ZnO/liter.

TABLE VIII

Increase in Capacity by Partial Discharge During Charge on Cells Which Have Been  
on Float and on Stand

Cell Number Separator: 6 layers SWRI-GX	103	104	112	113
Constructed:	5/18/67	5/18/67	5/23/67	5/23/67
Formation (5.5 ma/sq. in) started Amp hrs	6.21/67 5.80	5/21/67 5.80	5/26/67 6.15	5/26/67 6.15
First discharge Amp hrs	4.60	4.60	5.00	5.20
Recharge: (8.3 ma/sq. in) Amp hrs	4.11	4.27	5.60	5.20
Second discharge Amp hrs	4.60	4.60	5.09	5.16
Recharge (8.3 ma/sq. in) Amp hrs	4.60	4.50	5.3	5.0
Third discharge Amp hrs	4.30	4.50	5.1	5.4
Recharge Amp hrs	4.50	4.60	5.6	CP 1.96 v
Fourth discharge Amp hrs	4.20	4.60	5.80	-
Recharge: CP 1.96 v				

TABLE VIII (continued)

Increase in Capacity by Partial Discharge During Charge on Cells Which Have Been on Float and on Stand

Cell Number	103	104	112	113
Fifth discharge Amp hrs	-	5.08	-	-
All cells start CP 1.96 v float Stop float all cells	6/12/67 10/2/67			
Discharge Amp hrs	10/2/67 4.90	4.90	6.33	3.2
Recharge (6.5 ma/sq. in) Amp hrs	4.70	4.90	5.5	4.9
Discharge Amp hrs	OC	OC	OC	5.7
Recharge (8.3 ma/sq. in) Amp hrs				5.80
Cells open circuit From To	10/6/67 12/5/67	10/6/67 12/5/67	10/6/67 12/5/67	10/20/67 12/5/67
Open Circuit on 12/5/67 Discharged at 1.8 amp to remove Amp hr	1.859 0.20	1.860 0.20	1.860 0.18	1.860 0.18
Recharged at 5.5 ma/sq. in Amp hrs returned	1.58	1.45	1.08	0.74
Discharge 12/6/67 Amp hrs	5.90	5.90	6.54	6.39

TABLE IX A

Effect of Pre-formation Mode on Cell Pressures in Ag-Zn Cells Containing Compound 323-43

Cell Number	199	200	201	202	203	204
Pre-formation mode	CP 1.40 v	CP 1.40 v	CP 1.40 v	CP 1.50 v	CP 1.50 v	CP 1.50 v
Current limit (mo)	18	18	18	18	15	14
Hours	24	48	48	23	24	24
Final current (ma)	0.6	0.28	0.20	0.14	1.6	-
Final pressure (in Hg g)	-4.5	-2.1	-4.1	+5.4	+0.4	-3.5
Formation charge at 5.5 ma per sq. in (100 ma)						
Amp hrs	5.63	6.30	6.30	5.42	6.03	6.67
Pressure at end (in Hg g)	16.0	6.2	1.6	13.0	6.0	8.2
After partial cycle (0.9 amp hrs at 1.8 amp discharge; recharge at 100 ma)						
Net gain (Amp hrs)	1.65	1.05	1.01	1.26	0.94	0.51
After second partial cycle						
Net gain	-	-	-	0.50	0.50	-
Total Net Amp hrs charge	7.58	7.35	7.31	6.98	7.47	7.18

(1) Electrolyte for all cells: 35% KOH containing 75 gm ZnO per liter.

(2) Separation: 6 layers SWRI-GX.

(3) Pack tightness: 0.0026 in per layer of separator.

TABLE IX B

Effect of Pre-formation Mode on Cell Pressures in Ag-Zn Cells Containing Compound 325-45

Cell Number	205	206	207	208	209	210
Pre-formation mode	CP	1.50 v	(1) cc	(1) cc	(1) cc	(1) cc
Current limit (ma)	15	13	10	6	10	10
Hours	24	24	28	43	24.6	24
Final current (ma)	1.6	-	-	-	-	-
Final pressure (in.Hg g)	-	1.2	-3.0	-3.3	-2.1	-2.5
Formation charge at 5.5 ma per sq. in (100 ma)						
Amp hrs	5.65	5.77	4.58	6.03	5.51	5.34
Pressure at end (in.Hg g)	37.8	3.8	-0.5	5.0	2.0	13.8
After partial cycle (0.9 Amp hrs at 1.8 Amp discharge; recharge at 100 ma)						
Net gain (Amp hrs)	1.04	1.14	1.67	0.50	1.27	1.04
After second partial cycle						
Net gain (Amp hrs)	-	-	0.42	0.31	0.35	0.70
Total Net Amp hrs	6.69	6.91	6.67	6.84	7.13	7.04

(1) Currents are approximate varying as much as 3 ma.

(2) Electrolyte for all cells: 42% KOH containing 110 gm ZnO per liter.

(3) Separation: 6 layers SWRI-GX.

(4) Pack tightness: 0.0026 per layer of separator.



#### D. Replication of Cells with Consistently Low Internal Pressure

Knowledge had thus progressed to the point where it was felt possible to construct cells which would consistently have low gas pressure. Constructional details for a new group of four cells to show the degree of reproducibility which could be achieved were as follows:

- (1) Five layers of SWRI-GX separator (roll 83).
- (2) A separator allowance of 0.003" per layer.
- (3) Electrolyte - 40% KOH nearly saturated with ZnO.
- (4) Negative mix - 7% 323-43, 93% ZnO (no Teflon).
- (5) No pre-amalgamation of the negative silver grid.
- (6) A 28 hour slow pre-formation charge.

The 7-plate cells were vacuum filled and soaked in the flooded condition overnight. The electrolyte level was then adjusted to about 80% of the height of the plates.

Prior experience led us to believe that sealed cells constructed in this manner might still have low capacities due either to a PPO or an epoxy effect. Either effect was thought to be due to degradation products resulting when the organic material is digested in hot KOH during sterilization. To estimate the extent of these possible effects using the present cells which were made using PPO cases and shims, they were sterilized at 135°C for 108 hours unsealed in a stainless steel bomb. After sterilization they were sealed with Bondmaster 639 epoxy, fitted with pressure gages, and overpotted in larger cases. No epoxy was present during sterilization so that this variable was eliminated. The cells were formed and charged using a preformation rate of 0.55 ma/in<sup>2</sup> and a formation rate of 5.0 ma/in<sup>2</sup>.

Two cells developed no pressure whatsoever during formation or subsequent cycling. The other two developed oxygen pressure at the end of formation when the automatic equipment failed to cut out. This pressure was allowed to decay by recombination with the zinc electrodes before further cycling was carried out. No further pressure developed in these cells thereafter.

The first two cycles were conducted (see Table X) so that the data obtained could be compared with previous data. The third and fourth cycles included the new partial discharge which increased cell capacity as predicted.

TABLE X  
Capacities of High Performance  
Cells

Formation: Preformation of 12 ma for 28 hrs. Charge at 5 ma/in<sup>2</sup> to 2.04 v; Discharge at 77 ma/in<sup>2</sup> to 1.20 v

	<u>Cell I</u>	<u>Cell II</u>	<u>Cell III</u>	<u>Cell IV</u>
Single Stage Chg. Cap.	6.09 AH	6.48 AH	6.46 AH	6.55 AH
Single Stage Dischg. Cap.	4.37 AH	4.15 AH	4.45 AH	4.65 AH

Second Cycle: Charge at 7 ma/in<sup>2</sup> to 2.02 v; Dischg. first stage at 77 ma/in<sup>2</sup> to 1.20 v, Discharge second stage at 30.8 ma/in<sup>2</sup>

Single Stage Chg. Cap.	4.77 AH	4.57 AH	4.62 AH	4.59 AH
First Stage Dischg. Cap.	4.62 AH	4.51 AH	4.45 AH	4.84 AH
Second Stage Dischg. Cap.	0.36 AH	0.42 AH	0.52 AH	0.44 AH
Total Dischg. Cap.	4.98 AH	4.93 AH	4.97 AH	5.28 AH

Third Cycle: Charge at 7 ma/in<sup>2</sup> to 2.02 volts, partial discharge to 20% depth at 102 ma/in<sup>2</sup>, resume charge at 5.6 ma/in<sup>2</sup> to 2.02 volts. Dischg. at 102 ma/in<sup>2</sup> to 1.20 volts, then at 20.5 ma/in<sup>2</sup> to 1.20 v

First Stage Chg. Cap.	5.13 AH	4.99 AH	5.02 AH	5.27 AH
Second Stage Chg. Cap.	2.10 AH	2.20 AH	2.02 AH	2.96 AH
* Total Chg. Cap.	6.15 AH	6.11 AH	5.96 AH	6.35 AH
First Stage Dischg. Cap.	4.82 AH	5.20 AH	4.70 AH	5.10 AH
Second Stage Dischg. Cap.	0.76 AH	0.60 AH	0.78 AH	0.72 AH
Total Dischg. Cap.	5.58 AH	5.80 AH	5.48 AH	5.82 AH

Fourth Cycle: Charge at 7 ma/in<sup>2</sup> to 2.02 volts, partial discharge to 20% depth at 102 ma/in<sup>2</sup>, resume charge at 5.6 ma/in<sup>2</sup> to 2.02 volts. Discharge first stage at 102 ma/in<sup>2</sup> to 1.20 volts, discharge second stage at 20.5 ma/in<sup>2</sup> to 1.20 volts.

First Stage Chg. Cap.	5.36 AH	5.28 AH	5.08 AH	5.36 AH
Second Stage Chg. Cap.	1.69 AH	1.88 AH	1.81 AH	1.81 AH
* Total Chg. Cap.	5.93 AH	6.04 AH	5.77 AH	6.05 AH
First Stage Dischg. Cap.	5.06 AH	5.26 AH	4.80 AH	5.16 AH
Second Stage Dischg. Cap.	0.59 AH	0.70 AH	0.77 AH	0.72 AH
Total Dischg. Cap.	5.65 AH	5.96 AH	5.57 AH	5.88 AH

\* Net charge capacity - charge input less 20% partial discharge.

While the capacities of these cells sterilized in PPO cases are good and compare well with those of other sterilized cells, they are down about 20% when compared with the capacity of unsterilized sealed cells as shown in Table XI.

Also the capacity of cells sterilized in nickel containers and sealed in polystyrene cases with no contact with PPO or epoxy (series 389-40) suffer little or no capacity loss due to sterilization. Thus, it is concluded that the present cells which were not in contact with epoxy during sterilization must suffer from a PPO effect.

### III. EFFECTS OF ORGANIC CONSTITUENTS ON SILVER-ZINC CELLS

In order to study separately the effect of each organic constituent-adhesive, case material, and absorber - a new cell has been designed. (It is not easy to visualize a system in which the organic separator is eliminated unless inorganic types become available.) This design as shown in Figure 1, consists of a Teflon insert for the nickel bombs we have long used, into which the cell pack is placed. The nickel bomb is provided with insulated connections for the purpose of charging and discharging the cell without removing it from the bomb after sterilization. The combinations to be examined are as follows.

1. Control: Silver and zinc oxide plates, SWRI-GX separator.  
No epoxy adhesive, no PPO, no EM-476 absorber.
2. Like 1., but with cured epoxy chips present.
3. Like 1., but with PPO shims present.
4. Like 1., but with EM-476 present.

### IV. GRID SUPPORTS

In order to assist EMED in uncovering suitable metals to reinforce electrodes for shock resistance, the Research Center has undertaken some work in this area. Because of magnetic requirements, strength, chemical resistance, and electrical compatibility with the system, the choice of materials is severely limited. The first three requirements make zirconium and Inconel prime candidates. The following discussion concerns the effect of these materials on cell capacities and gas pressure during cycling following sterilization. As a screening test, overvoltage studies and corrosion tests were conducted on the grids, and finally cells were constructed using some of these materials.

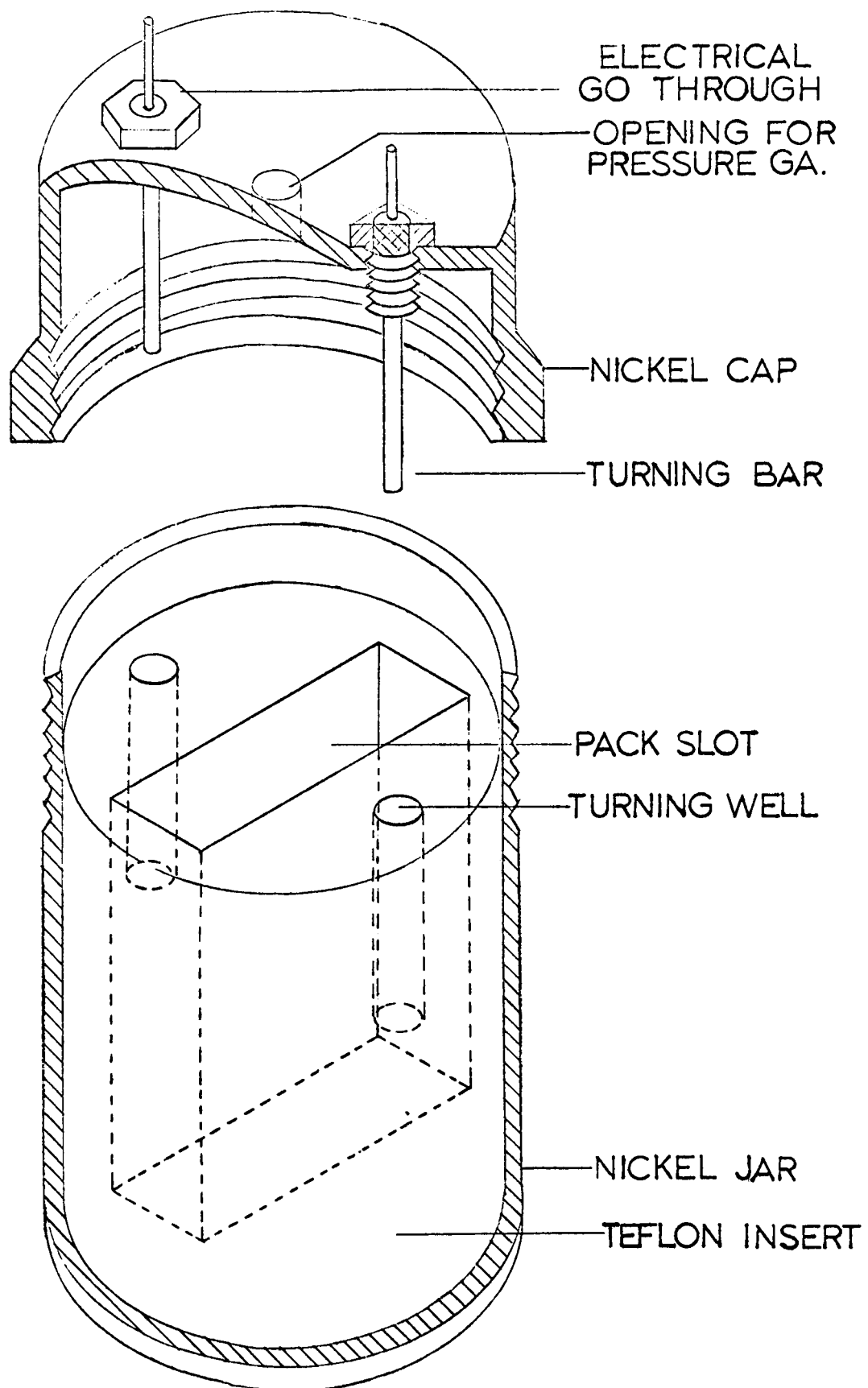
#### A. Positive Plate Grid Supports

One of the first tests was designed to compare the current flow in various positive electrode-grid configurations while they were being floated at constant potential. The grid configurations used were as follows:

TABLE XI  
Capacity of Various Series of Sealed Ag-Zn Cells in the  
Presence of Organics

Series	434-49 Cells 1 thru 4	389-40 Cells 16 thru 20	389-93 Cells 7 thru 12	389-93 Cells C-1 and C-2	434-16 Cells 17 and 18
Condition	Steril. in PPO cases	Steril. - no PPO or Epoxy	Steril. PPO and Epoxy	Non steril. controls Steril. PPO shims	
Avg. Capacity	Avg. Cap. AH/gram Ag	Avg. Cap. AH/gram Ag	Avg. Cap. AH/gram Ag	Avg. Cap. AH/gram Ag	Avg. Cap. AH/gram Ag
1st cyc.	4.40 AH	3.4 AH	3.04 AH	3.55 AH	4.50
2nd cyc.	4.60 AH	3.5 AH	2.55 AH	3.74 AH	4.59
Description:					
Series 434-49	7-plate; negative mix 93% ZnO, 7% comp. 323-43; 5 layers SWRI-GX with 0.003" allowance; electrolyte -40% KOH plus 103 g ZnO/l; sterilized in PPO cases then sealed with Bondmaster 639 epoxy.				
Series 389-40	5-plate; negative mix-91% ZnO, 7% comp. 323-43, 2% Teflon; 5 layers RAI-110 with 0.004" allowance; electrolyte -43% KOH plus 115 g ZnO/l; sterilized in nickel containers and transferred to polystyrene cases and sealed.				
Series 389-93	5-plate; negative mix-91% ZnO, 7% comp. 323-43, 2% Teflon; 5 layers RAI-110 with 0.004" allowance; electrolyte -43% KOH plus 115 g ZnO/l; sealed with DEN-438EK85 epoxy in PPO cases and sterilized.				
Series 389-93 Controls	Same as series 389-93 but not sterilized.				
Series 434-16	7-plate; negative mix -93% ZnO, 7% comp. 323-43; 5 layers SWRI-GX with 0.002" allowance; electrolyte -40% KOH plus 103 g ZnO/l; sterilized in nickel containers with PPO shims and then sealed in polystyrene cases with Bondmaster 639 epoxy.				

FIGURE 1  
TEFLON CASE IN NICKEL BOMB



- (1) A single expanded silver grid.
- (2) A sheet of zirconium sandwiched between two expanded silver grids.
- (3) A sheet of silver-plated zirconium sandwiched between two expanded silver grids..
- (4) A sheet of Inconel sandwiched between two expanded silver grids.
- (5) A sheet of silver-plated Inconel sandwiched between two expanded silver grids.

Each of the above constructions had silver powder pressed into both faces and sintered in place. After sterilization at 135°C for 120 hours, the test electrodes were wrapped in sausage casing separators and placed in open cases with nickel oxide antipodes. The electrolyte was 40% KOH nearly saturated with ZnO. The electrodes were charged at constant current (35 ma) for 70% of their theoretical capacity. The charging was then completed at a constant potential of 1.5 volts. After the electrodes were fully charged, the float current was measured and all currents were nearly alike and small (about 1 ma per plate) showing that no appreciable current was producing gas.

The electrodes were weighed before and after and, since no change occurred, the conclusion of this test was that very little, if any, plate corrosion took place.

#### B. Overvoltage Study of Grid Support Materials

Grid support materials treated in various ways as shown in Tables XII and XIII were run at various currents in 40% KOH to determine HgO reference overvoltages. These two tables show electrode potentials versus a Hg-HgO reference electrode at two current settings. The test was run to determine which electrode support would have the highest overpotential as a positive and as a negative electrode.

As a negative electrode amalgamated silver gave the best results, and silver plated Inconel was second best. The untreated and oxidized samples of zirconium were best as positive electrodes. Those samples which had the highest absolute potentials would generate the least amount of gas while on charge.

#### C. Cells with Zirconium Grid Supports

Four cells were constructed using a silver plated zirconium support plate in the positive, and an oxidized zirconium support plate in the negative in order to determine the possible effects of these on the Ag-Zn system. Other constructional details for this group of sealed 7-plate cells are as follows:

TABLE XII  
Overpotentials of Negative Grid Supports

<u>Support Metal</u>	<u>Support Treatment</u>	Potential *	
		<u>20 ma</u>	<u>100 ma</u>
Zirconium	none	-1.47 v	-1.63 v
Zirconium	oxidized	-1.46	-1.70
Zirconium	silver plated	-1.22	-1.40
Zirconium	silver plated and amalgamated	-1.29	-1.45
Inconel	none	-1.21	-1.33
Inconel	previously charged one hour	-1.45	-1.60
Inconel	silver plated	-1.50	-1.76
Inconel	silver plated and amalgamated	-1.26	-1.39
Silver	none	-1.44	-1.58
Silver	amalgamated	-1.76	-1.87
Cadmium	none	-1.44	-1.61
Cadmium	amalgamated	-1.46	-1.64

\* Potential between the support metal and a Hg-HgO reference electrode at the two current levels shown. The electrode area was 6.55 in<sup>2</sup>.

TABLE XIII  
Overpotentials of Positive Grid Supports

<u>Support Material</u>	<u>Support Treatment</u>	Potential *	
		<u>20 ma</u>	<u>100 ma</u>
Zirconium	none	+1.08 v	+1.30 v
Zirconium	oxidized	+1.07	+1.28
Zirconium	silver plated	+0.75	+0.91
Zirconium	silver plated and amalgamated	+0.75	+0.88
Inconel	none	+0.56	+0.61
Inconel	silver plated	+0.80	+0.87
Inconel	silver plated and amalgamated	+0.75	+0.89
Silver	none	+0.81	+0.91
Silver	amalgamated	+0.84	+0.92
Cadmium	none	+0.81	+1.10
Cadmium	amalgamated	+0.30	+1.03

\* Potential between the support metal and a Hg-HgO reference electrode at the two current levels shown. The electrode area was 6.55 in<sup>2</sup>.



- (1) Five layers of SWRI-GX separator.
- (2) A separator allowance of 0.003" per layer.
- (3) Electrolyte - 40% KOH which was then nearly saturated with ZnO.
- (4) Negative mix - 7% 323-43, 93% ZnO, (no Teflon).
- (5) No pre-amalgamation of the negative silver grid.

After these cells were vacuum filled and soaked in the flooded condition overnight, the electrolyte level was adjusted to 80% of the height of the plates. Sterilization was performed in a large bomb with open PPO cases at 135°C for 108 hours, and sealing was accomplished with Bondmaster 639 epoxy after sterilization.

The cells were charged using an initial rate of 12 ma per cell followed by 97.5 ma to 2.02 v. They were then given a 20% discharge at 2A and re-charged at 110 ma to 2.02 v. All four cells developed pressure (> 40 psig) and by the fifth discharge the pressure was over 140 psig.

The discharges were carried out in two stages. They were first discharged at 2A to 1.30 V and then at 0.4A to 1.30 v. The data are shown in Table XIV. In addition to the high pressures slightly low capacities were obtained from these cells and it is concluded that cell performance is somewhat hurt by the oxidized zirconium supports. Because the hydrogen overvoltage on oxidized zirconium is lower than that of amalgamated silver grid, it is probable that hydrogen was being produced at the same time that ZnO was being reduced. Therefore not as much zinc is available for discharge as would normally be the case. Since sealed cells are zinc limiting on discharge, this explanation would account for both the gas generated and the capacities observed.

Previous experiments have shown that oxygen recombines readily in this cell design. Since these cells maintained their pressure on stand overnight, the gas must have been hydrogen. Cells are now on formation which contain the same type of silver-plated zirconium supports in the positives as the cells which developed pressure but with normal negatives. The results of this experiment should indicate which electrodes were involved in gas production and whether silver plated zirconium supports can be used in positive electrodes to encourage adhesion of the active silver to the grid support.

## V. ABSORBER STUDIES

The capacity test for absorbers (which involves using a limited amount of electrolyte) was performed on a sample of asbestos obtained from Raybestos-Manhattan, Inc. This absorber, Novabestose 7401, was reported to maintain its structure and be usable after sterilization in KOH at 135°C. The

TABLE XIV  
Capacity (AH) of Sealed Cells with Zr Supports  
in Both Plates

First Cycle Cell No.	Chg.		Total chg.	Dischg.		Mid- voltage	Dischg.		Total Dischg. *	AH/g Ag
	1-stage	2-stage		1-stage	2-stage		1-stage	2-stage		
Zr-1	1.90	1.93	3.83	2.12	0.49	1.40 v	2.12	0.49	2.61	0.21
Zr-2	2.30	1.43	3.73	2.12	0.26	1.40 v	2.12	0.26	2.38	0.19
Zr-3	2.11	1.77	3.88	2.06	0.36	1.40 v	2.06	0.36	2.42	0.19
Zr-4	2.56	2.04	4.60	2.76	0.41	1.40 v	2.76	0.41	3.17	0.25
Second Cycle										
Zr-1	2.74	1.35	4.09	2.24	0.46	1.39 v	2.24	0.46	2.70	0.22
Zr-2	2.76	1.24	4.00	2.24	0.25	1.40 v	2.24	0.25	2.49	0.20
Zr-3	2.79	1.20	3.99	2.20	0.28	1.40 v	2.20	0.28	2.48	0.20
Zr-4	3.52	1.22	4.74	2.68	0.35	1.40 v	2.68	0.35	3.03	0.24
Third Cycle										
Zr-1	2.41	1.01	3.42	2.36	0.39	1.39 v	2.36	0.39	2.75	0.22
Zr-2	2.31	0.86	3.17	2.26	0.23	1.40 v	2.26	0.23	2.49	0.20
Zr-3	2.36	0.80	3.16	2.30	0.23	1.40 v	2.30	0.23	2.53	0.20
Zr-4	2.39	0.81	3.20	2.66	0.32	1.40 v	2.66	0.32	2.98	0.23
Fourth Cycle										
Zr-1	2.90	0.96	3.86	2.44	0.40	1.41 v	2.44	0.40	2.84	0.23
Zr-2	2.75	0.87	3.62	2.48	0.26	1.42 v	2.48	0.26	2.74	0.22
Zr-3	2.82	0.84	3.66	2.48	0.28	1.42 v	2.48	0.28	2.76	0.22
Zr-4	3.01	1.08	4.09	2.86	0.28	1.42 v	2.86	0.28	3.14	0.25

\* The active silver was light in these 7-plate cells. Thus the capacity should be multiplied by 1.4 for comparison with other 7-plate cells using EMED positives.

data as shown below indicate that this absorber is as good as but no better than the control which was Kendall Mills EM 476. After cycling, the cells were taken apart and the asbestos absorber indeed did maintain its structure. Results of the capacity test are as follows:

	0.003" Asbestos			0.005" Asbestos			EM-476		
Cycle	1	2	3	1	2	3	1	2	3
Capacities (AH)	2.22	2.40	2.22	2.36	2.44	2.28	2.10	2.25	2.34

For some time now it has been suspected that some of the unusual discharge characteristics of heat sterilizable Ag-Zn cells are due to the use of Kendall Mills' EM-476 polypropylene material as absorbers or retainers. When 41% KOH electrolyte is used in loosely packed cells, the capacity decreases between the first and second cycle and then tends to increase during the following cycles. This does not happen when 35% KOH is used.

The decrease in cell capacity occurring during the second discharge is not a reflection on the charge input during the first recharge since this is nearly always greater in amp-hrs than the first discharge. A possible explanation is that during the recharge, considerable zinc metal is deposited within the fibers and/or outside of the polypropylene retainer. During the subsequent discharge this metal is unavailable for discharge because of loss of electrical contact with the major portion of the active material. The amount of metal so deposited might be expected to be less in the lower electrolyte concentration, and in the more tightly packed cells, since in the latter, the polypropylene retainer fibers would themselves be more tightly compacted. To study this, it was decided to use separator material as zinc electrode retainers. Only one cell has been constructed, in this manner, and tested, No. 229 (Table IV B). The drop in capacity during the second discharge did not occur. Electrolyte concentration was 41% KOH, pack tightness value  $2.5 \times 10^{-3}$  in. per layer of separator, and 3% Compound 323-43. No polypropylene absorber was included around the silver electrode. Electrolyte level was at the top of the electrodes at the end of formation. Cell capacity was improved especially when a high rate discharge was employed. This method of cell construction will be investigated further during the next quarter.

## VI. MIXING OF ACTIVE MATERIALS

For some time the question of the degree of mixing of the zinc oxide electrode materials has been raised. Our work with earlier electrodes indicated considerable variations as far as overvoltages were concerned, and although a quantitative correspondence was not achieved there were some indications that the amount of gas formed in gassing tubes could be correlated with the amount of protection indicated by the Tafel plots. Recently we began using a new batch of negative mix but it proved to be non-homogeneous to the naked eye and light microscopy. The finished electrodes from this batch were scrapped since we believe that this is a potential cause of gassing.

However, before the non-homogeneous sample was obtained some experiments were started to determine if the time of mixing was important. The materials used were 7% Compound 323-43 and 93% ZnO, all of which had passed 325 mesh as received. They were mixed for 1, 2, 4, 8, 30 and 180 minutes in a 4 qt. PK blender with an intensifier bar which had a speed of about 1900 rpm. The shell speed was about 24 rpm. Samples taken at the end of each mixing period were given to the Crystallography Section for visual observation. Their report stated that all samples appeared to be well mixed with no distinguishable differences from portion to portion. It was also pointed out that 30 min. of mixing was the best length of time and anything longer was superfluous.

Table XV shows the results from overvoltage study.

One would expect the same set of numbers from electrodes that offer the same overvoltage protection. Although most of these values are about in the same range it is clear that good mixing was not achieved. For example, one pair of samples taken after four minutes of mixing, 4 and 4' and another pair, 8 and 8' taken after eight minutes gave Hg-HgO reference voltages over the current range of 10 to 100 ma of 1.50-1.76v, 1.49-1.53v, and 1.64-1.78v, 1.48-1.52v respectively. It is interesting to note that after 1 minute mixing the range was 1.52-1.78 v which was about the same as any other longer mixing times.

The results imply that visual methods or microscopy are not sufficiently sensitive to judge good mixing for this application and that the overvoltage method shows promise and requires more work.

TABLE XV  
Overvoltage Data on the Mixing Time of Negative Materials

Current (mA)	Potentials (volts) of electrodes of samples mixed for various times (minutes)													
	1 min.		2 min.		4 min.				8 min.		30 min.		180 min.	
	1	1'	2	2'	4	4'	8	8'	30	30'	180	180'		
10	1.52	1.53	1.52	1.52	1.50	1.49	1.64	1.48	1.52	1.54	1.50	1.52		
20	1.67	1.68	1.66	1.63	1.66	1.49	1.70	1.48	1.67	1.66	1.60	1.62		
40	1.73	1.73	1.71	1.72	1.70	1.495	1.73	1.48	1.71	1.72	1.62	1.70		
60	1.75	1.75	1.74	1.75	1.73	1.50	1.75	1.49	1.74	1.74	1.74	1.72		
80	1.77	1.76	1.75	1.77	1.74	1.51	1.77	1.49	1.76	1.76	1.76	1.74		
100	1.78	1.78	1.76	1.78	1.76	1.53	1.78	1.52	1.76	1.78	1.78	1.76		

## FABRICATION AND TESTING OF CELLS

### I. FABRICATION AND TESTING OF 25 AH CELLS

#### A. Objectives and Summary of Work to Date

Design goals for this task were the development and test of non-magnetic 25-50 AH sealed Ag-ZnO (or Ag-CdO) cells capable of wet heat sterilization at 135°C for 120 hours, charge, pre-flight test, 8 month charged life (on float or charged stand) during a space flight, a planet landing impact of  $2800 \pm 200$  g from  $113 \pm 2$  ft. per second in any axis, and 4-cycles after landing.

Previous work has developed through five generations of sealed cells, each having design stress analysis, process development for the new heat sterilizable materials, cell manufacture, and shock tests at JPL. Conclusions to date are:

- Plate active materials are not capable of supporting their own weight, even when fully charged, during impact in the  $\pm y$  and  $\pm x$  axis.
- Damage of positive active material increases with increasing plate thickness and becomes acute in thick plates desirable for high operating energy density.
- Plates must be heavily reinforced with central cores with high tensile strength and stiffness factors. Metals, not plastics, must be used.
- Thick wall PPO 531-801 cell jars can be sealed with epoxy by a massive cover assembly, designed to lock in place all plate core structures, and survive 2,000-2,400 "g" impact in 5 AH size cells.
- Stress analyses can predict failure modes provided assumptions are correct and material strengths are not degraded beyond expectations by heat sterilization.

#### B. Plate Support Structures

Pertinent physical properties of metals considered for central plate cores are summarized in Table XVI. Of these metals all but Inconel 600 have been eliminated for use in the 25 AH cell. Nickel is magnetic. Titanium and zirconium gas by reaction with cell electrolyte at 135°C. Copper and Be Cu

TABLE XVI

## PROPERTIES OF PLATE REINFORCING MATERIALS

Item	Pure Silver	Titanium Comm. Pure	Nickel	Inconel 600	Beryllium Copper	Coin Silver	Zirconium Unalloyed	Copper
Tensile Strength (psi) Hard annealed	54K 27K	80K (Ti-75A) 35K (Ti-35A)	103K 65K	120K 94K	175K --	60-70K --	90K 65K	40K --
Yield Strength (psi) Hard annealed	44K 8K	70K 25K	97K 23K	110K 37K	130K --	-- --	35K 10 - 15K	-- --
Modulus E. (psi)	10X10 <sup>6</sup>	16x10 <sup>6</sup>	30x10 <sup>6</sup>	31x10 <sup>6</sup>	19x10 <sup>6</sup>	11x10 <sup>6</sup>	14x10 <sup>6</sup>	17x10 <sup>6</sup>
Density, gm/cc #/in <sup>3</sup>	10.5 .379	4.5 .164	8.9 .321	8.5 .304	8.2 .297	10.4	6.5 .233	8.9 .321
Magnetic Susceptibility	-.2x10 <sup>-6</sup>	3.2x10 <sup>-6</sup>	> 1000	400x10 <sup>-6</sup>	-.45x10 <sup>-6</sup>	-.02x10 <sup>-6</sup>	1.3x10 <sup>-6</sup>	-.08x10 <sup>-6</sup>
Electrical Resistivity	1.6	50	9.5	98.1	10.0	1.8	40	1.7
$\mu$ , cm								
Anneal Temp °F	400	850-1300	1500	1300°F	1400	500	1300	700/1200
Stiffness Factor E/W-in.	204	450-700	800	700	750	260	700	360/650
	26.4x10 <sup>6</sup>	98x10 <sup>6</sup>	93x10 <sup>6</sup>	104x10 <sup>6</sup>	64x10 <sup>6</sup>	--	59x10 <sup>6</sup>	53x10 <sup>6</sup>
Tensile Strength per Unit Density Hard Anneal	142x10 <sup>3</sup> 71x10 <sup>3</sup>	490x10 <sup>3</sup> 210x10 <sup>3</sup>	320x10 <sup>3</sup> 201x10 <sup>3</sup>	395x10 <sup>3</sup> 310x10 <sup>3</sup>	590x10 <sup>3</sup> --	-- --	385x10 <sup>3</sup> 279x10 <sup>3</sup>	124x10 <sup>3</sup>

## NOTES:

1. Pure silver begins to anneal at about 400°F (204°C)
2. The higher the number the more ferromagnetic. Negative numbers indicate diamagnetic materials. (Permeability less than one.)
3. Coin silver begins to anneal at about 500°F (260°C). There are various palladium & silver alloys with & without copper which can be made very strong (up to 190K). These could be investigated. Low hydrogen overvoltage problems might be overcome by silver plating.

contaminate cell with cupric ion during heat sterilization. The silver metals do not have high enough stiffness factor. Present development is directed at cell designs where the negative plate will be reinforced with Ag plated Inconel cores and framed with PPO. The JPL membrane may be cemented to the frame or wrapped around it. Positive active material will be spot-welded and sintered to a Ag plated Inconel core. Both plates will slide into slots machined or molded into the jar inner walls. The most advanced design is the 3/4 frame cell design, the Model 365.

#### C. High Impact-Heat Sterilizable 25 AH 3/4 Framed Cell Design

Two feasibility test cells are in production. Ten mil thick Inconel 600 sheet Ag plated over a very thin nickel flash will be the structure for each plate. The feasibility cells will be a 3 plate version: one full inner negative and two outer half positives. Each plate will be 3/4 framed-down each side edge and across the bottom with PPO frames cemented to the Inconel core and then to the inner jar wall. Impact forces will thus be distributed along the entire frame to wall bond as well as the struts epoxied into walls in the cell cover.

Negatives will have 5 layers of SWRI-GX membrane (irradiated polyethylene) cemented to the PPO frame as the sole negative active material retainer and cell separator system. This epoxy bond will be crucial to design success. Dow epoxy DEN438-EK85/DMP-30 was used to cement successively 5 L of membrane to PPO 531-801 frames. The assembly was successfully heat sterilized submerged in cell electrolyte for 120 hours at 135°C. Sections of the frame were then given pull tests. The membrane to frame bond failed at the membrane-epoxy interface at 8-10 pounds pull per inch of width when pulled in the shear direction. Such a low bond strength is not desirable. In the cell the cemented area will be twice the test area above and calculations show this strength will suffice.

Epoxy to Inconel bonds are now being evaluated. Initial tests show a reduction in bond strength from 600 psi to 200 psi tensile shear during heat sterilization of double lap test specimens. Again, this average strength all around the frame will be adequate, provided shock forces are distributed uniformly around the entire frame, and provided the expansion coefficient difference (Inconel 600,  $9 \times 10^{-6}/^{\circ}\text{F}$ ; PPO 531-801,  $29 \times 10^{-6}/^{\circ}\text{F}$ ) does not break the bond during sterilization.

After the 3/4 frame design has been proven feasible to meet both heat sterilization and high impact, a production cell design with molded parts will be tested.

#### D. Ag-Boron Composites

ESB has reviewed the recent literature on boron filament-metal composites and obtained samples of Ag-boron composites from General Technologies



Corporation, Reston, Virginia. Strengths of the order of Inconel, the conductivity of silver, and the chemical compatibility of Ag in both positive and negative plates appear to be available. This material is an expensive back-up to the Inconel 600 plate support designs and will be investigated further.

## II. HEAT STERILIZABLE-HIGH IMPACT 5.0 AH CELLS

### A. Objectives

In this task ESB is required to develop a 5.0 AH cell capable of wet sealed heat sterilization for 120 hours at 125°C and after charge a simulated landing impact of  $2800 \pm 200$  "g" from  $113 \pm 2$  ft./sec.

### B. Engineering Models

Cell design, the ESB Model 344, has been described previously (1). During the time required to obtain molded cell case parts three cell packs were assembled, sealed in fabricated jars, charged and shock tested with no prior heat sterilization. Shock directions, impact velocities, stopping distances, and peak "g" levels are given in Table XVII. Loaded voltages were measured on each cell before and after shock as a measure of shock damage. Figure 1 shows up to 180 mv drop at 20 amps for +Y and +X axis and 260 mv drop at 20 amps for the -Y axis. Discharge capacities immediately after shock, measured by a two step discharge at 5 amps then 1 amp, decreased 36.2%. Capacity loss was greatest in the -Y axis, confirming the voltage drop test. The cell shocked in the X axis shorted on the charge after shock. Dissection showed the failure mode was buckling of the weaker silver struts supporting the negative plates with some twisting of the titanium positive toward the buckled negatives. Table XVIII gives discharge capacities of the three cells before shock and the two surviving cells after shock. On the first recharge after shock cell capacities recovered the 36% loss and exceeded the pre-shock capacity by 8%. Capacity losses are attributed to loss of contact between negative active material and the negative grid recovered by charge. The surviving cells completed eleven cycles before end of life. This experiment verified the desirable stiffness factor and tensile strength of titanium (for non-sterile cells) and stressed the need for reinforcement against buckling of silver plate supports.

### C. Prototype C-SAD Cells: Heat Sterilization, Cycling, and Shock Tests

Prototype Model 344 cells, incorporating all silver sheet plate supports and molded PPO 531-801 cell cases, subcovers, and cell covers, were next developed for heat sterilization and shock tests. Cell sealing techniques

- (1) Interim Summary Report, JPL Contract 951296, Period  
September 24, 1965 to September 30, 1967, Task VIII, page 175.

TABLE XVII  
SHOCK DATA FOR MODEL 344 TEST CELLS

Cell S/N	Weight (gms)	Impact Velocity (fps)	Stopping Distance (in.)	Shock Duration (msec)	Average "g" Load	Peak "g" Load
3	488	110	0.780	--	2890	--
4	483	114	0.836	1.1	2890	3500
5	483	115	0.866	1.1	2840	3200

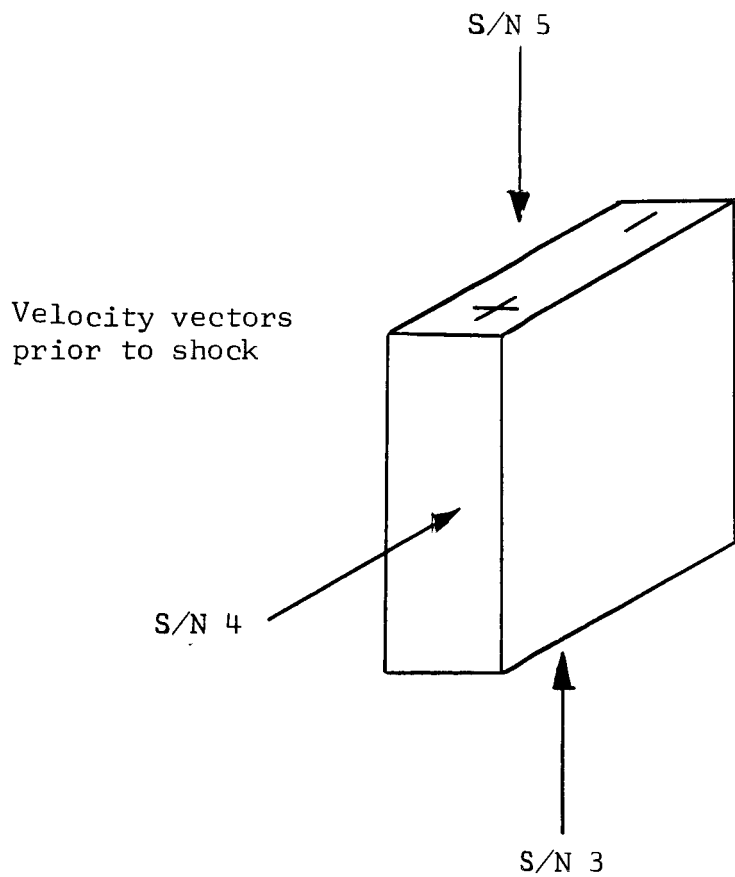
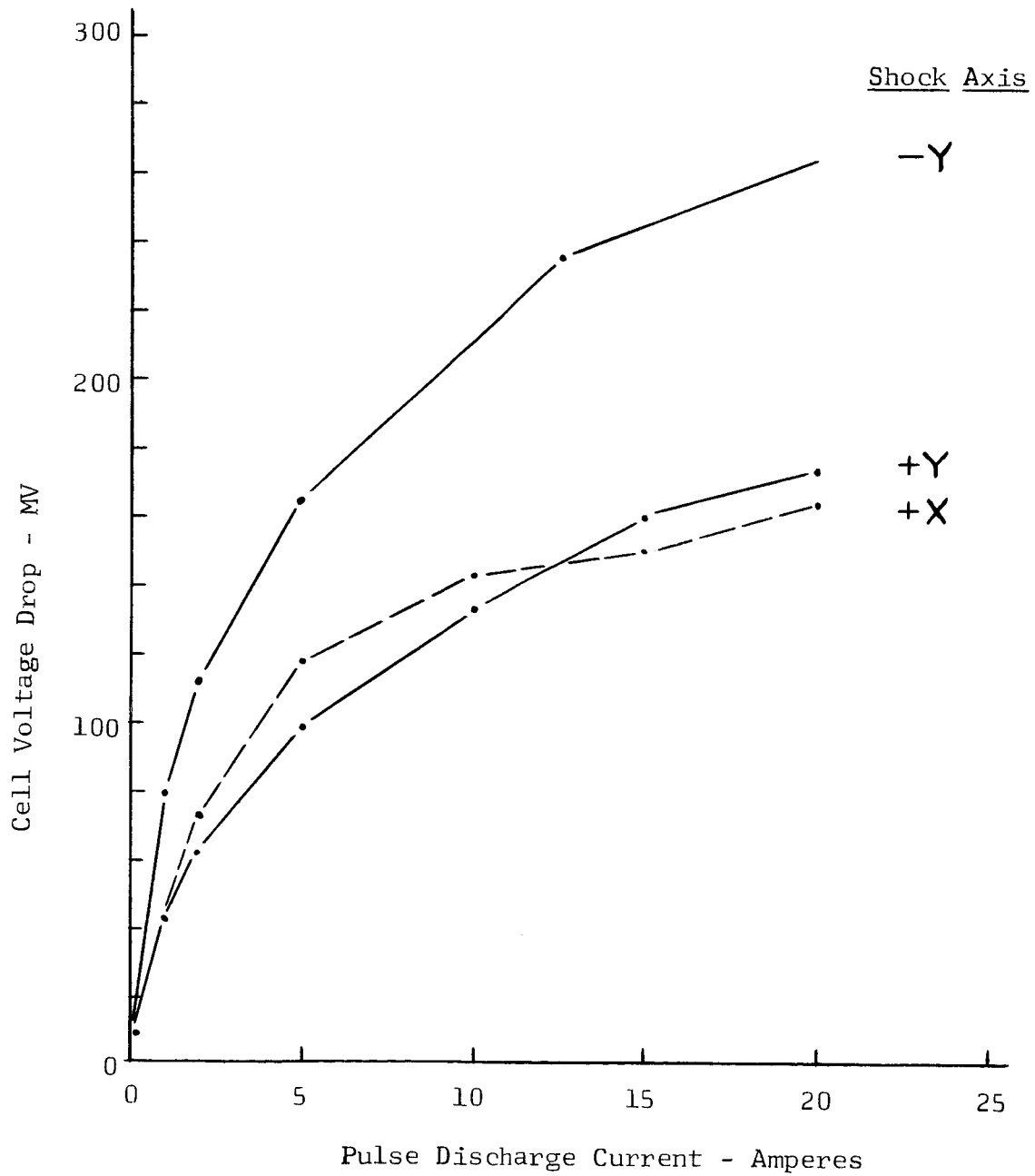


TABLE XVIII

EFFECT OF 2800 "G" IMPACT ON CAPACITY  
IN 5 AH SEALED NON STERILE CELLS

Test History	Cycle No	Discharge Capacity AH	Mean Capacity AH	Loss From Shock, %
Formation Discharge	1	6.13, 6.40, 6.66	6.40	
First Cycle Shock After Full Charge	2	4.61, 4.84, 5.08	4.84	0
Discharge After Shock	3	2.68, 3.20, 3.39	3.09	-36.2
Recharge, Then Discharge Second Cycle After Shock	4	4.93, 5.60	5.27	+8.2
Recharge, Then Discharge Third Cycle After Shock	5	4.41, 5.17	4.79	-1.0

FIGURE 1  
DECREASE IN LOAD VOLTAGE  
FROM 2870 "G" SHOCK ON  
5 AH CELLS



and the cell cover design were verified by burst tests of four sealed cases using hydrostatic pressures. Pressures at burst unsupported were 150, 160, 160, and 170 psig: i.e.  $160 \pm 24$  psig  $\bar{X} \pm 3$  s. Two assemblies tested without the overlapping top cover burst at 60 psig which demonstrated the value of the cap design to improve seal strength.

#### D. Heat Sterilization

Eleven cells were assembled, sealed, and heat sterilized sealed for 120 hours at 125°C. Each cell was clamped in 1/8" sheet steel along its broad faces just to the actual cell thickness dimension. Copper tubing spacers over the clamp through bolts prevented excessive clamping pressure. The cells were then overpotted with RTV-11 silicone rubber to prevent oxidation (darkening) of the PPO 531-801 container during sterilization in air. Under these conditions all cells passed the heat sterilization test with no electrolyte leakage.

#### E. Electrical Cycling and Impedance Tests

A. C. impedance tests of all cells, made with a Keithley Model 502 milliohmmeter, showed internal impedance variation from 230 to 560 mohm before heat sterilization and 35 to 71 mohm after heat sterilization. After charge the impedance range was 11 to 22 mohm. Table XIX summarizes a.c. impedances measured during cycle 1 and 2. For charge the sample was divided into two groups by a.c. impedance: Group I was closely matched in the range 460 to 560 mohm; Group II was closely matched in the range 230 to 300 mohm with one outlier at 540 mohm. Each group was charged in series at a constant potential of 1.38 volts per cell to convert all the negative additive quantitatively before forming zinc metal.

One cell in each group became a low voltage outlier and the other cells rose in voltage to the 1.46 - 1.47 volt range. Each outlier was removed and placed on a separate charger. All cells then charged successfully through the CP portion of formation. Neither outlier could have been predicted by pre-heat sterilization impedances. All cells then completed the constant current portion of charge to a test end voltage of 2.02 volts per cell. Table XX summarizes charge and discharge capacities after heat sterilization with plateau, peak voltages and calculated efficiencies. Figure 2 shows the drastic loss of capacity from heat sterilization of the hermetically sealed cells when compared to the control cells. Cells surviving shock and heat sterilization approach the capacity of control cells by the 8-10th cycle. The effect of shock in the +Y, -Y, and -X axis in the range 2400 to 3100 "g" is given in Table XXI. The mean effect of shock over all axis and "g" levels on discharge capacity vs. no shock cells obtained from the data of Table XX may be summarized.

TABLE XIX  
EFFECT OF HEAT STERILIZATION AND CYCLING ON A.C.  
IMPEDANCE OF 5.0AH SEALED CELLS

Test Time	Measured Impedance by Serial Number, mohms												Mean N=11
	Charge Group I					Charge Group II							
	High Impedance					Low Impedance							
	11	12	13	14	19	7	8	9	10	15	17		
1. Before HS	560	500	500	460	460	250	240	340	230	540	300	398	
2. After HS	46	46	46	71	52	35	43	43	36	44	42	46	
3. After formation charge	18	14	16	15	11	16	22	20	15	16	15	16	
4. Before discharge 1	20	18	20	18	20	16	22	20	15	16	15	18	
5. After discharge 1	20	16	22	19	22	22	23	23	21	25	17	21	
6. Before charge 2	20	16	22	19	22	22	23	23	21	25	17	21	
7. After charge 2	18	13	12	20	16	15	21	26	15	13	14	17	

TABLE XX

OPERATING CAPACITIES AND VOLTAGES AFTER HEAT STERILIZATION  
120 HOURS AT 125°C  
MODEL 344 5.0 AH CELLS

Test	Chg. Group I High Impedance					Chg. Group II Impedance						Mean n = 11
	11	12	13	14	19	7	8	9	10	15	17	
1. Formation Chg. AH	6.11	7.71	6.39	7.36	7.28	7.15	7.05	7.94	7.15	6.26	7.13	7.02
2. Theoretical Chg. Efficiency, %	53	67	58	64	63	62	61	69	62	54	62	61
3. Discharge Capacity												
@ 5 A	2.30	4.05	2.90	3.52	3.47	4.02	3.75	4.96	3.62	2.84	4.17	3.60
@ 1 A	1.02	0.41	0.19	0.75	0.31	0.60	0.34	0.98	0.83	0.77	0.97	0.65
Total, AH	3.32	4.46	3.09	4.27	3.78	4.62	4.09	5.94	4.45	3.61	5.14	4.25
4. Efficiency (4) %	54	54	46	58	52	65	58	75	62	58	72	65
5. Voltage, Volts												
5A plateau	--	1.46	1.42	1.43	1.43	1.44	1.44	1.46	1.44	1.42	1.43	1.44
1A peak	1.53	1.52	1.53	1.52	1.53	1.53	1.53	1.52	1.53	1.53	1.53	1.53
6. Second Cycle Charge Input AH	3.88	5.36	4.28	4.77	4.89	4.62	4.51	5.15	4.40	3.55	4.73	4.55
7. Efficiency (4)	117	120	138	112	129	100	110	87	99	98	92	109
8. Net Input, AH	6.67	8.61	7.88	7.86	8.39	7.15	7.52	7.15	7.10	6.21	6.72	7.39
9. 2nd Cycle Output	**			**								
@3.3A	1.48	4.49	3.94	2.80	4.49	4.20	3.94	4.49	3.74	2.91	3.94	n = 9
@0.7A	0.50	0.54	0.20	0.30	0.34	0.20	0.45	0.34	0.54	0.54	0.34	
Total AH	1.98	5.03	4.14	3.10	4.83	4.40	4.39	4.83	4.28	3.45	4.28	
10. Net Input, AH	(S) due to shock	3.58	3.74		3.56	2.75	3.13	2.32	2.82	2.76	2.44	3.01
11. 3rd Cycle Input, AH		5.07	4.20		4.91	4.41	4.19	4.86	4.20	3.58	4.33	4.42
12. Efficiency, %		101	101		102	100	96	101	98	103	101	
13. Net Input, AH		8.65	7.94		8.47	7.16	7.32	7.18	7.02	6.34	6.77	7.42
14. 3rd Cycle Output		**				**			**			
@3.3A		3.30	3.00	3.30	5.31	3.30	4.38	5.44	2.80	3.40	2.80	
@0.7A		0.07	0.43	0.29	0.35	0.23	0.33	0.39	0.52	0.44	0.16	
Total: AH		3.37	3.43	3.59	5.66	3.53	4.71	5.83	3.32	3.84	2.96	
15. 4th Cycle Output						(S)						
@3.3A		4.62	4.24	4.06	4.18	due	3.24	5.65	at	3.46	4.50	
@0.7A		0.24	0.25	0.33	0.24	to	0.34	0.46	JPL	0.46	0.18	
Total: AH		4.86	4.49	4.39	4.42	shock	3.58	6.11		3.92	4.68	
16. 5th Cycle Output						(S)						
@3.3A		4.95	4.30	at	3.55	due	5.22			2.62	5.60	
@0.7A		0.25	0.36	JPL	0.33	to	0.33			0.29	0.26	
Total: AH		5.20	4.66		3.88	shock	5.55			2.91	5.85	
17. 6th Cycle Output												
@3.3A		at	3.04		3.43			5.74		(S)	(S)	
@0.7A		JPL	0.21		0.57			0.48				
Total: AH			3.25		4.00			6.22				
			(S)					(S)				
18. Life at Short:	1.0	3.0	2.1	5.30	--	1.0	1.8	2.1	3.0	2.1	1.8	

(1) Formation discharge: 5A to 1.30V, then 1A to 1.30V.

(2) All other discharges: 3.3A to 1.30V, then 0.7A to 1.30V.

TABLE XX

OPERATING CAPACITIES AND VOLTAGES AFTER HEAT STERILIZATION  
120 HOURS AT 125°C  
MODEL 344 5.0 AH CELLS  
(Continued)

- (3) 2800 "g" impact at JPL on cells S/N 7, 10, 11, 12, 14, 17.
- (4) Output/Input X 100.
- (5) Net Input = all inputs less all outputs.
- (\*\*) Discharge cycles preceded by JPL pulse test of 5 second currents of 2, 5, 10, 20, 30, and 40 amps plus 5 amps for 2 minutes.



FIGURE 2

CAPACITY LOSS FROM WET HEAT STERILIZATION  
AND HIGH IMPACT IN 5 AH CELLS

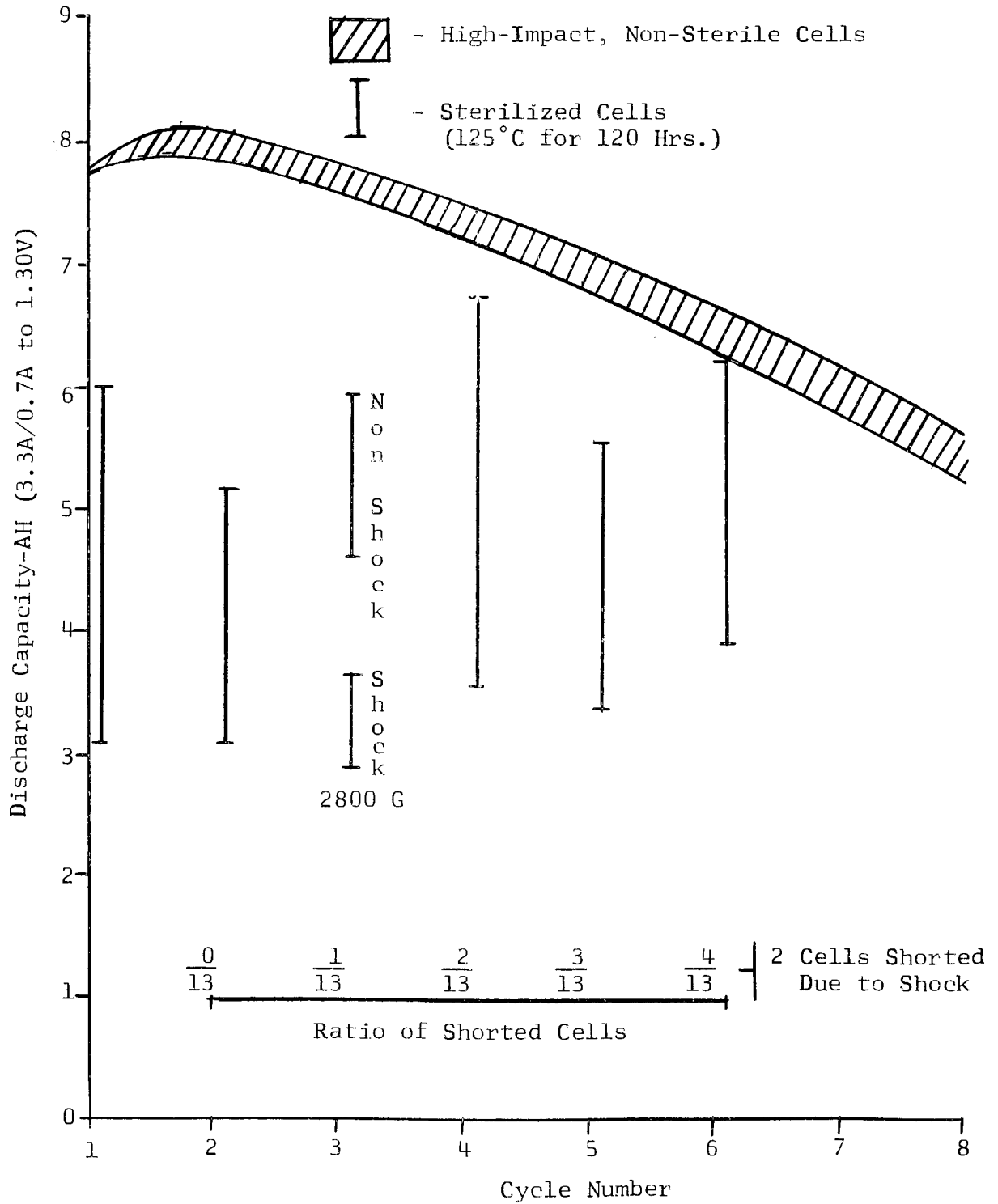


TABLE XXI

EFFECT OF HIGH IMPACT ON MODEL 344 5 AH CELLS

S/N	Velocity Axis	Stopping Distance (in)	Shock Duration (msec)	Mean "g" Load	Peak "g" Load	Loaded Voltage Drop, Mv			Discharge Capacity AH		
						5A	10A	20A	30A	3.3A	0.7A
10	+y (terminals forward)	1.000	--	2,410	--	29	46	73	76	2.80	.52
7		0.755	1.0	3,050	3,600	29	45	67	180	3.30	.23
12	-y (terminals aft)	0.970	1.2	2,460	--	29	37	47	73	3.30	.07
17		0.785	--	3,115	--	23	31	40	57	2.80	.16
14	-X	1.035	1.5	2,380	--	31	47	71	68	2.80	.30
11	(+ terminal edge forward)	0.780	1.0	3,150	3,500	233	188	77	--	1.48	.50
Summary of Mean Effects on Capacity Out at 3.3A Rate											
Axis		S (2 cells)		Shock Load		S (3 cells)					
+y		6.10		2,400 "g"		8.90					
-y		6.10		3,100 "g"		7.58					
-X		4.28									

Test Condition	Sample n	Discharge Capacity, AH			
		3.3A	0.7A	Total	Range
No Shock	5	3.95	0.38	4.33	1.38
Shock	6	2.75	0.30	3.05	1.55
Shocked Cells After Recharge	3	4.14	0.24	4.38	1.27
Shock Loss %		-30	-27	-30	

Post shock examination of the six shocked cells revealed no damage to any cell container or epoxy seal. X-rays of the cells before and after shock showed that the plate struts of cells buckled severely at 3,050 "g" in the terminals forward direction, but only slightly at the smaller 2410 "g" level. A conclusion can thus be reached that the Model 344 cells, as presently manufactured, can survive 2000-2400 "g" shock in the terminals forward direction, but plate struts must be stiffened by replacement of the silver sheet with Inconel, or with Ag-boron composite structures before a 2800  $\pm$  200 "g" shock can be overcome reliably.

#### F. Redesigned Prototype C-SAD Cells

Prototype cells have been redesigned in the following areas:

- Increase in electrolyte per cell to eliminate dry condition observed on dissection of engineering cells.
- Reinforcement of plate struts with polysulfone shims to prevent buckling during shock in the terminals forward direction.
- Addition of DEN438-EK85/DMP-30 epoxy to depth of 0.060" in bottom of jar to cement cell pack to bottom of jar.

Four samples of lot P-116 RAI membrane and lot 120 SWRI-GX membrane were tested for 40% KOH electrolyte absorption during heat sterilization to verify this proposed mechanism for electrolyte level change. Table XXII unit electrolyte absorption increases 9.4% for RAI-116 and 21% for SWRI-GX material. For the Model 344 cell a reduction of 2.9 cc electrolyte would be expected by this phenomena from a total electrolyte volume of 19.5 cc. Two cells were fabricated with clear polysulfone windows cemented into the PPO jars to permit a visual observation of electrolyte level. In this way a final electrolyte volume per cell of 22.0 cc was found

TABLE XXII

ELECTROLYTE ABSORPTION OF STERILE AND NON-STERILE SEPARATOR LOTS  
(RAI-116 AND SWRI-GX)

Lot No.	Dry Thickness (Mils)	Wet Thickness (Mils)	Thickness Change (%)	Change Roll Direction (%)	Change Across Roll (%)	Dry Wt. Per Dry Area (gm/in <sup>2</sup> )	Wet Wt. Per Dry Area (gm/in <sup>2</sup> )	Wet Wt. Per Wet Area (gm/in <sup>2</sup> )	Porosity (%)	Unit KOH Absorption
RAI P-116 (unsterilized)	3.12	4.60	47	3.40	3.60	0.0264	0.0690	0.0648	39	1.60
RAI P-116 (sterilized)	2.08	3.82	84	1.85	6.50	0.0262	0.0727	0.0668	49	1.75
GX-120 (unsterilized)	1.42	2.38	66	4.0	11.50	0.0182	0.0578	0.0498	62	2.18
GX-120 (sterilized)	1.60	3.15	97	-5.50	8.00	0.0204	0.0740	0.0724	73	2.64

- (1) Heat Sterilization - 108 hours at 135°C.  
 (2) Data above is average of four samples for each lot.  
 (3) Porosity (%) =  $\frac{\text{Electrolyte Volume of Wet Sample}}{\text{Total Volume of Wet Sample}}$   
 (4) Unit KOH Absorption =  $\frac{\text{Electrolyte Weight in Wet Sample}}{\text{Weight of Dry Sample}}$   
 (5) All tests performed in 40% KOH.

to give a level just above the plate tops before sterilization and just below after sterilization.

A second mechanism for electrolyte level change is water loss through the PPO 531-801 case. Four Model 344 cell cases were sealed per drawing with 23.5 cc 40% KOH in each cell. Each was supported by 1/8" steel plates across their broad sides beneath the seal area. Two cases were overpotted with RTV-11 silicone rubber to the base of the top cover to simulate encapsulation in a chassis. One cell case contained a polysulfone window to permit visual observation of electrolyte levels. During 120-124 hours heat sterilization at 135°C no leaks were observed. Weight losses are given in Table XXIII with calculated loss rates and concentration changes. This mechanism thus accounts for 1.0 - 1.5 cc additional water loss during 120 hours at 135°C, or a total loss all causes of 3.9 - 4.4 cc.

Nine cells are now being assembled for shock tests at JPL. Seven will contain strut reinforcements and the epoxy pack hold down. Two will be controls identical to the Engineering model cells except for polysulfone windows in the cell. Weight analyses of the eleven cells at seal show electrolyte weights of 31.0 - 32.3 gm (21.6 - 22.5 cc) for the controls and 27.6 - 28.5 gm (19.2 - 19.8 cc) for the prototype cells. The difference in weight is traceable to the lower free volume in the prototype cells occupied by the epoxy hold down. In all cells electrolyte level was adjusted to be just above plate tops before heat sterilization.

Heat sterilization and shock tests on the prototype cells are scheduled for the coming quarter.

#### G. Production Cells

JPL released ESB to manufacture 40 Model 344 cells, identical to the Engineering models except for the amount and type of electrolyte. This lot of cells was activated with 22.0 cc of 40% KOH with 91 g/L ZnO, allowing 0.75 cc per cell for water loss, sealed, and shipped to JPL on 11 January 1968 as system test cells.

The only production problem encountered was alignment of the pinned plate struts in the subcover seal. This problem was solved by elongating the holes 20 mils in the  $\pm$  X shock axis.

Tests at JPL will include heat sterilization after assembly as a 12-cell battery, formation charge and discharge, preflight cycling, and a drop test in the C-SAD spacecraft.

### III. DEVELOPMENT OF HEAT STERILIZABLE HIGH IMPACT 5 AND 25 AH BATTERIES

#### A. Objective

In this 18 month program ESB is required to design, develop experimental

TABLE XXIII

## WATER LOSS FROM MODEL 344 CELLS DURING HEAT STERILIZATION

Sample No	Sterilization		Observed Weights-gms				Loss Rate mg Hr	Final Concentration KOH %
	Temperature °C	Time Hrs	Initial Electrolyte	Initial H <sub>2</sub> O (calc)	Final H <sub>2</sub> O (calc)	Loss H <sub>2</sub> O		
1	125	120	36.42	21.86	20.69	1.17	9.8	41.5
2	135	124	38.91	23.35	21.81	1.54	12.4	41.7
		216			20.75	2.60	12.0	42.8
3	135	124	39.45	23.65	22.55	1.10	8.9	41.2
		216			21.81	1.84	8.5	41.9
4	135	124	39.17	23.50	22.41	0.99	8.0	41.1
		216			21.64	1.76	8.2	41.8

\* Samples 1 & 2 were not overpotted with RTV-11. Sample 1 contained PS window.  
 Samples 3 & 4 were not overpotted with RTV-11.  
 No evidence of KOH loss. No carbonation.

\*\* Diffusion area: 11.2 in<sup>2</sup>  
 Diffusion wall thickness 0.10 in.

cells, a dummy battery, a prototype battery, and manufacture four 24 volt qualification batteries of two sizes to meet the performance requirements of JPL Specification GMP-50437-DSN-C. The more difficult design and performance objectives are:

- Landing impact of  $2800 \pm 200$  "g" from  $115 \pm 2$  ft/sec.
- Heat sterilization 120 hours at  $135^{\circ}\text{C}$ .
- Power output of 300 W after nine months in space.
- Energy density of 25 WH/lb at two capacities:  
120 WH, 5 AH battery and 600 WH, 25 AH battery.

#### B. Summary of Work to Date

The 5.0 AH cell being developed for the C-SAD spacecraft will become the cell for the 120 WH battery of this task and the 25.0 AH cell (3/4 framed plates) developed under Section I. Fabrication and Testing of 25 AH Cells will become the cell for the 600 WH battery. A 23-59% capacity loss during heat sterilization, now observed on the 5.0 AH high impact design, is attributed to:

- Chemical deterioration at  $135^{\circ}\text{C}$  of EM-476 polypropylene absorbers.
- Volatiles from epoxies or PPO 531-801.
- Excessive absorption of electrolyte by GX membrane.

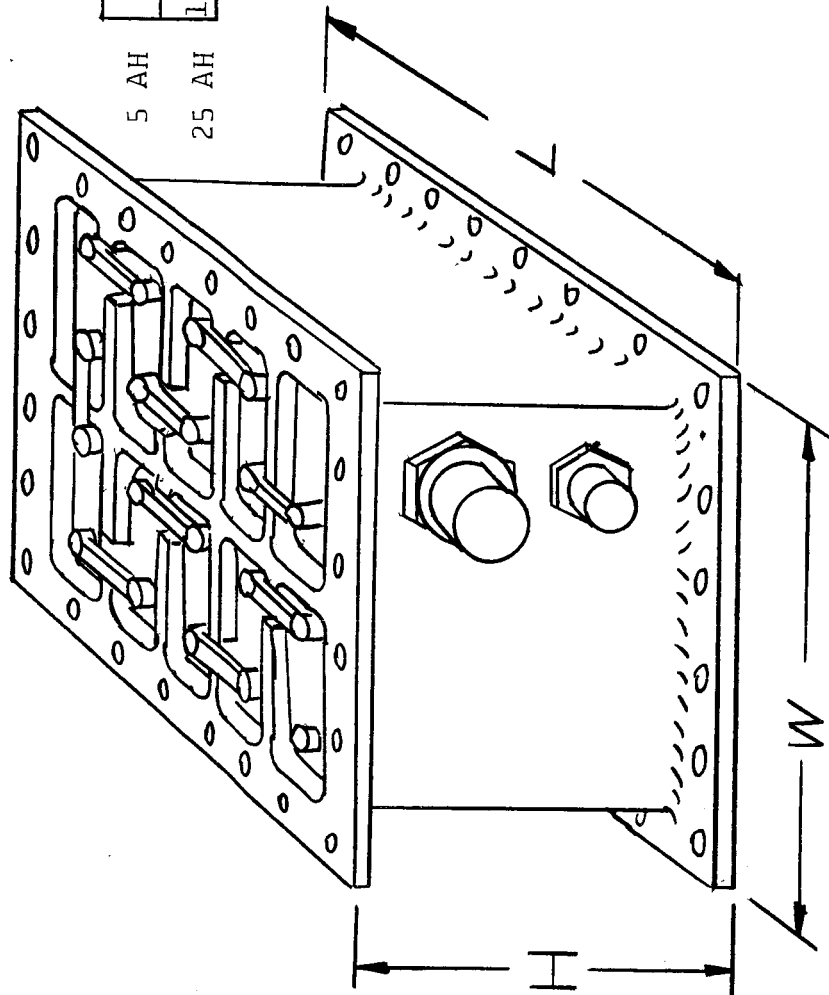
Non-impact five ampere-hour size cells are now being constructed in the variations: with and without EM-476 retainer, two primary epoxy sealants with minimum exposure to electrolyte, DEN438-EK85/DMP-30 epoxy sealant exposed in 0, 1.6, 3.2, and  $4.3 \text{ in}^2$  per cell, two other epoxies exposed at  $3.2 \text{ in}^2$  area level, and two membranes (SWRI-GX and RAI-116).

Design of batteries has begun. Figure 3 presents a typical chassis now being evaluated in stress and weight analysis. Two such 9-cell units would be connected in series to form the 18 cell 5 AH or 25 AH 24 volt batteries. Size and weight estimates are preliminary but are based on existing performance and will improve as capacity losses in heat sterilization and after shock are corrected. Flange mounting at top and bottom of battery will permit between deck installation. All exposed intercell connections will be potted over with a silicone or epoxy sealant. Thermal coefficients of expansion will be matched as closely as possible in this selection.

#### IV. DEVELOPMENT OF HEAT STERILIZABLE NON IMPACT HIGH CYCLE LIFE 1200 WH BATTERY

FIGURE 3

TYPICAL DESIGN OF HIGH IMPACT  
5 AH AND 25 AH BATTERIES  
NINE-CELL UNIT  
2500 G SHOCK



Wt.	L	W	H	Wh/lb.
8.3	7.00	5.50	4.00	7.8
16.8	8.75	8.30	6.50	19.2

WALL THICKNESSES:

Outer -	.12	.25
Inner -	.06	.06

Cell Capacity: 5AH 25AH



### A. Objectives

This 30 month development program requires design, test, and manufacture of four qualification 18-cell 1200 watt-hour batteries per JPL Specification GMP-50436-DSN-B and capable of:

- Cycle life of 400 50% depth cycles after heat sterilization, nine months of interplanetary travel, and a soft landing on Mars.

### B. Summary of Work to Date

ESB has developed a PPO 531-801 case and epoxy seal for a 25 AH heat sterilizable non-high impact cell. Two control cell packs for initial tests were sealed in this jar, heat sterilized 120 hours at 125°C, and then discharged at rates from the 0.2 C rate to the 1.0 C rate through eight cycles. Figure 4 compares discharge capacities of a Model 345 heat sterilized cell and a non-heat sterilized cell. No capacity loss from heat sterilization was observed. Figure 5 shows discharge curves at varying rates for a similar cell after HS. Table XXIV outlines the design parameters to be investigated beginning in the next quarter. A subcontract has been negotiated with R. J. Hader and Arnold H. E. Grandage of the School of Experimental Statistics, North Carolina State University for consulting services in design of experiments and statistical interpretation of the data.

Eight cycling circuits have been assembled. Initial cell tests are scheduled for cycling at 100% depth (25 AH rated capacity) 3 hr D/21 hr. C/ then 50% depth (12.5 AH) 3 hr. D/9 hr C.

## V. DEVELOPMENT OF HEAT STERILIZABLE 200 "G" IMPACT 2000 WH BATTERY

### A. Objectives

In this 12 month program ESB will design, test, and then manufacture four heat sterilizable 24 volt 80 AH qualification batteries meeting the requirements of JPL Specification GMP-50607-DSN for delivery in September 1968.

### B. Work to Date

Cell design is complete. Test cells have been released to be manufactured by the Engineering Pilot Plant. Figure 5 is a schematic view of the cell. Table XXV summarizes the estimated performance. The cell cases have been molded successfully in PPO 534-801. Machined covers sealed to the case with epoxies are being evaluated for failure mode and burst pressures. To eliminate any possible degradation during heat sterilization no

FIGURE 4

PERFORMANCE OF 25 AH HEAT STERILIZABLE  
NON-IMPACT CELLS

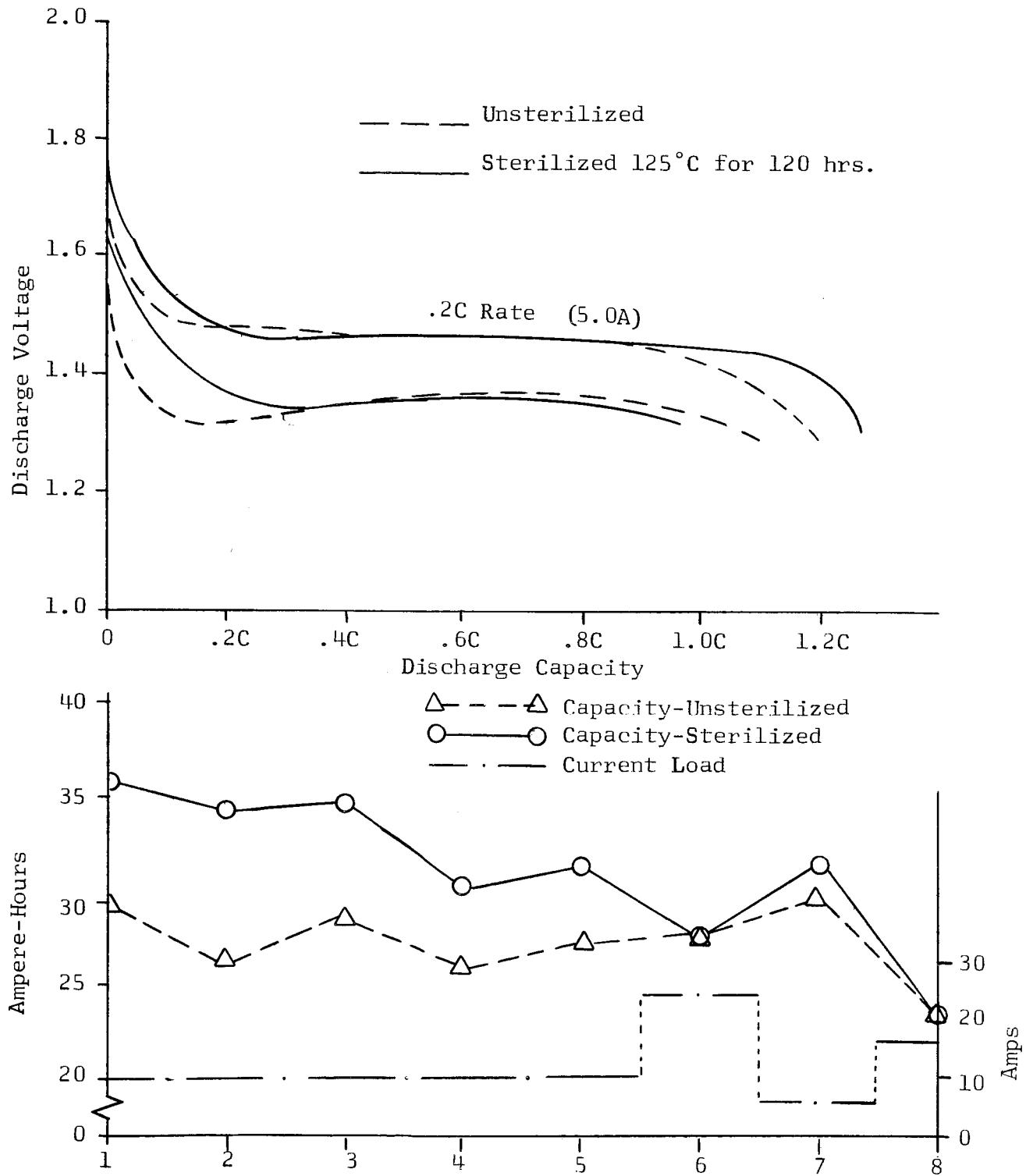


FIGURE 5

EFFECT OF DISCHARGE RATE ON PERFORMANCE  
OF 25 AH STERILE, SEALED CELL  
(HEAT STERILIZED 120 HOURS AT 125°C)

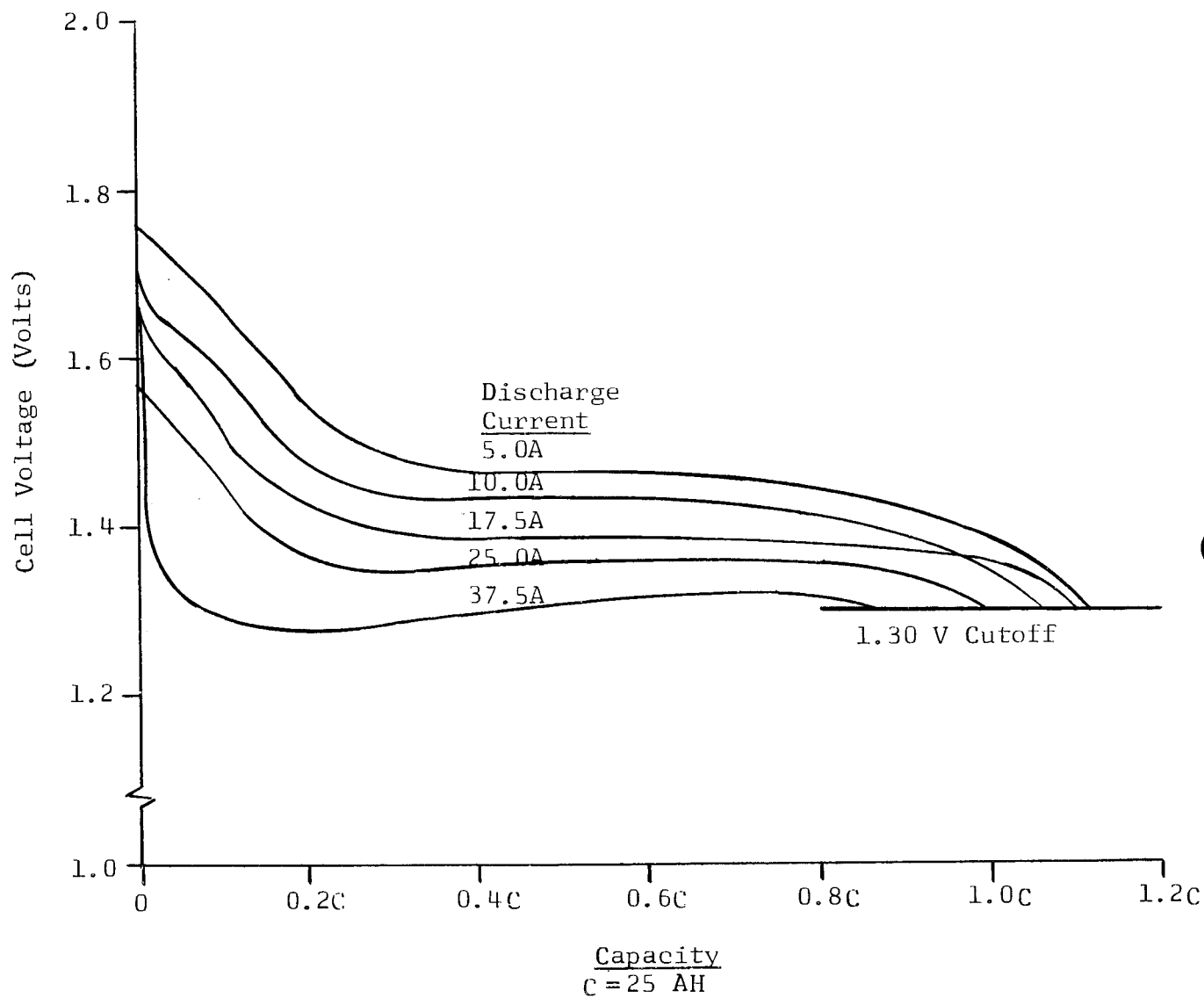


TABLE XXIV

EXPERIMENTAL HSS48 CELL TEST VARIABLES

NEGATIVE PLATE

- BINDER - TEFLONATED, % USED
- DENSITY -
- ADDITIVE - ESB CPD 323.43, % USED

POSITIVE PLATE - DENSITY

- NO. LAYERS SWRI-GX MEMBRANE
- MEMBRANE WRAP - POS. OR NEG.
- ABSORBER - TYPE & LOCATION

ELECTROLYTE

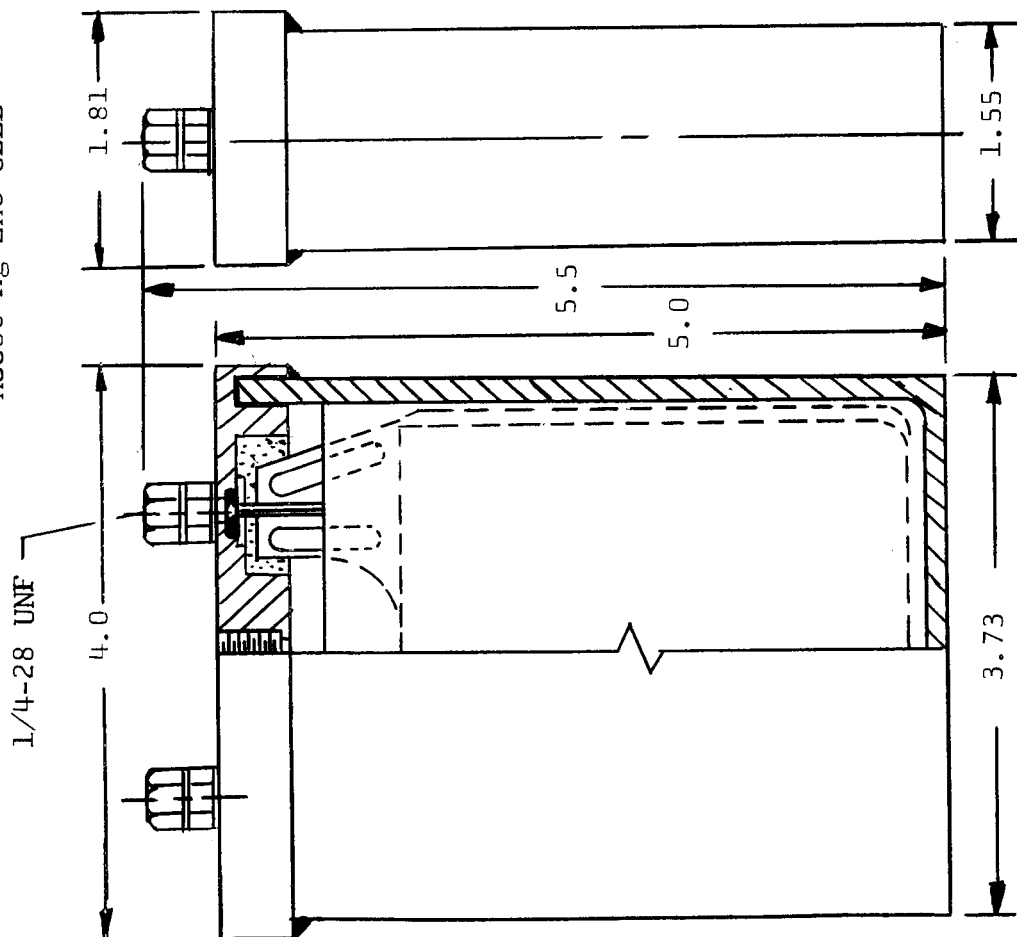
- CONCENTRATION
- ADDITIVES
- VOLUME (LEVEL)

CELL PACK

- RATIO - ZnO/Ag
- PACK TIGHTNESS
- PLATE SIZE

FIGURE 6

DEVELOPMENT MODEL 364  
HEAT-STERILIZABLE  
HSS80 Ag-ZnO CELL



Predicted cell performance  
at C/4 discharge rate:

Voltage, Avg.	1.38 V
Capacity	80 AH
Energy	108 WH
Energy Density	40 WH/lb.
Weight	2.7 lb.

TABLE XXV

WEIGHT ANALYSIS AND ESTIMATED OUTPUT  
80 AH HEAT STERILIZABLE 200 "G" IMPACT CELL  
ESB MODEL 364

<u>Cell Component or Characteristic</u>	<u>Material</u>	<u>Weight (gm)</u>
1. Active Plate Materials		
Positive	Ag	286
Negative	ZnO Mix	204
2. Plate Structure	Ag	168
3. Separator Membranes, 6L	SWRI-GX	39
4. Cell Case & Cover	PPO 534-801	165
5. Epoxy Sealant		26
6. Electrolyte	38% KOH Sat. ZnO	235
7. Hardware, Misc.		<u>55</u>
Total:		1178 (2.6 lb)
8. Average Voltage at C/4 Rate, Volts		1.39
9. Capacity at C/4 Rate, AH		80
10. Energy Output at C/4 Rate, WH		111
11. Energy Density, WH/lb		43
12. Dimensions: L (overall)		1.8
(Inches) W		4.0
H		5.5
13. Volume: in <sup>3</sup>		39.6

polypropylene negative plate retainer or positive plate absorber will be used. The separator system will be simply six layers of SWRI-GX membrane.

Battery chassis design to support the cells for the 200 "g" impact and heat sterilization cell pressures has been completed and released to procurement. Cell encapsulants and shims to support the cell cases for heat sterilization are now being evaluated. Final materials selected will be used to pot a set of dummy cells (sealed cases containing electrolyte) into the prototype chassis in April to evaluate cell seals through the destructive forces of heat sterilization and 200 "g" impact tests. Prototype cell and battery design will be released in late April for manufacture in May and testing in June and July.

Present estimates give battery weight of 60 pounds and overall dimensions including flanges:

H, in.	6.0
W, in.	8.0
L, in.	19.0
Volume, in <sup>3</sup>	912

At a projected energy output of 2000 WH after heat sterilization energy densities are estimated to be 35.0 WH/lb. and 2.2 WH/in<sup>3</sup>. The JPL requirement is 35 WH/lb. in the voltage range 22.5 to 33.5 volts at a power output of 500 watts.

APPENDIX I  
SEPARATOR QUALITY ASSURANCE TESTS

In supporting quality assurance tests, ESB has evaluated the physical properties of 10 lots of Southwest Research Institute GX membrane and 13 lots of Radiation Application RAI-116 membrane. Table XXVI gives the mean and  $\pm 3$  sigma range for each of the six test variables. SWRI-GX membrane is in every case less variable.



TABLE XXVI  
Physical Characteristics Heat Sterilizable Membranes

<u>Test</u>	<u>Unit</u>	<u>SWRI-GX</u> <u>X</u> <u>+ 3 s</u>	<u>RAI-116</u> <u>X</u> <u>+ 3 s</u>
1. Lots Tested	n	10	13
2. Thickness, Dry	mils	1.7	2.2
Wet	"	2.2	2.8
3. Weight, Dry	mg/in <sup>2</sup>	22	25
Wet	"	50	58
4. Dimensional Change			
L (Roll)		+6	+5
W	%	+8	+4
T		+36	+32
5. Electrolyte Absorption G/G		1.6	1.6
6. Porosity	%	60	57
7. Pore Diameter	A°	2.2	2.9

Test Method ESB-MS-263 (31% KOH)

## CONCLUSIONS

1. A low current pre-formation charge of about 0.55 ma per square inch carried out over a period of 28 to 33 hours prior to starting normal formation has proven successful in virtually eliminating pressure build-up previously encountered.
2. Discharging about 20% of the capacity at the end of any normal charge and re-charging raises the subsequent discharge capacity about 15% above that obtained by a normal charging method.
3. However, even the application of the technique described in 2. above is not sufficient to offset the loss in capacity which is observed after sterilization of a sealed cell. At present it is believed that this capacity loss is principally associated with degradation products of one or more of the organic components of the system.
4. Sealed high impact 5 AH cells have been developed and are now capable of surviving impact in all axes in the range 2,000 - 2,400 "g". Decrease in discharge capacity may be as high as 30% on discharge after shock but is 100% recoverable on next cycle.
5. Heat sterilization of sealed 5 AH cell for 120 hrs at 125°C gives a capacity loss in the range 23-59%. Charge input and discharge output are decreased.
6. Stress analysis shows that larger 25 AH cell will require special plate supports to survive  $2800 \pm 200$  "g" shock.

## FUTURE WORK

1. Efforts will be continued to discover which components (case material, adhesive, absorber, or separator) contribute to capacity loss after sterilization of sealed cells.
2. New 5 AH cell designs call for substitution of SWRI-GX for EM-476 absorber and retainer in an attempt to avoid capacity loss after sterilization. These cells will also contain more rigid metals such as Inconel instead of silver sheet plate reinforcements so that the required 2600 - 3000 "g" shock resistance can be achieved.
3. The next design for the high impact 25 AH cell will use Inconel plate reinforcement framed on both sides and the bottom with PPO struts cemented in place with epoxy. It is expected that this construction, assembled into a rigid stack will withstand the  $2800 \pm 200$  "g" shock, though at a sacrifice of energy density.